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Issued August 8, 1908.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF SOILS—BULLETIN No. 52.

MILTON WHITNEY, Chief.

ABSORPTION BY SOILS.

BY

HARRISON E. PATTEN AND WILLIAM H. WAGGAMAN.

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LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Soils,
Washington, D. C., February 13, 1908.

Sir: I have the honor to transmit herewith the manuscript of a technical paper entitled Absorption by Soils, by Messrs. Harrison E. Patten and William H. Waggaman of this Bureau.

In accordance with your suggestion, the manuscript has been submitted to Assistant Secretary Hays, who concurs with me in recommending it for publication as Bulletin 52 of the Bureau of Soils.

Respectfully,

Milton Whitney,
Chief of Bureau.

Hon. James Wilson,
Secretary of Agriculture.

PREFACE.

In the present bulletin Messrs. Patten and Waggaman have brought together the literature covering absorption of dissolved solids from liquid solutions, together with results of some important experimental investigations which have been carried on in this laboratory in continuance of the general work on soil absorption which has been under way for several years. The importance of this subject for practical soil work, for fertilizer manufacture, and for various technical processes has long been known, but it is only within the past few years that its importance has become generally recognized.

The principal object of this work has been to determine how absorption controls the concentration of the soil solution, which is the great nutrient medium upon which plants feed, and, further, to determine the effect of absorption upon the structure of the solid portion of the soil in modifying its power to hold and maintain the soil solution for the continued use of the plant. As a result of this work it has been shown that a number of modifying factors enter into each particular case, which makes it impracticable to formulate a simple general law which will account quantitatively for the distribution of a dissolved substance between the liquid solution and the absorbing medium, although it is brought out very clearly that under the ideal conditions, where there is no change in the surface of the absorbing medium, a simple mathematical law can be predicated a priori, which law is approximately realized in practice in those cases where it is known that the least amount of change takes place in the absorbing surface. The nature of these modifying factors, and in a general way the extent to which they enter, with especial reference to soil components, has been the subject of careful investigation, the results of which are here recorded.

In general it may be said that our knowledge of the nature and character of absorption factors and their influence upon the concentration of soil solution, and upon the reactions which take place between soil components and artificially added constituents, has been materially advanced, and that the further investigation of this important line of soil studies will be more easily and more rapidly prosecuted on the basis of the work presented in this bulletin.

Frank K. Cameron.

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ABSORPTION BY SOILS.

INTRODUCTION.

From the standpoint of soil chemistry the absorption of material from air and from soil solution is of the first importance. The absorptive power of the soil enables it to retain the soluble salts necessary to plant life in spite of the leaching effect of rains, thus storing up soluble material from the weathering and dissolving soil grains for future needs of crops. Also it prevents the soil solution from becoming too concentrated.

Besides this holding back of nutrient soluble salts, the absorptive power of a soil has an important part in determining its physical condition. There is a relation between the quantity of soluble salts absorbed by the soil and the size and compactness of the soil-grain aggregates; and upon the size and arrangement of these soil aggregates, in turn, the optimum water content of the soil depends. The openness of a soil determines its ventilation, and thus likewise its opportunity for securing proper oxidation and for the forming of humus. The optimum water content[a] as determined by plant growth coincides in general with the percentage of moisture at which the soil has its maximum volume, and at this maximum the soil also shows its greatest openness or minimum resistance to root penetration. Thus a purely physicochemical reason is at hand for the existence of an optimum water content in soils, and we are now able to correlate several of the factors which determine the state of a soil known as "good physical condition." Likewise, through its absorptive power the soil removes from soil solution and soil atmosphere the waste products thrown off by growing roots,[b] which products are detrimental or inhibitory to continued growth.

Appreciation of these relations has come about gradually. Sand filters for purification of sea water and impure drinking water have been used at least since the time of Aristotle; the removal of salts from sea water by percolation through sand or earth filters was practiced in Bacon's day. Dr. Steven Hales announced to the Royal Society in 1739 that the first portion of sea water passed through stone cisterns was pure. Berzelius filtered salt solutions through sand and found that the salt content was more or less removed; and Matteucie determined the concentration of salt in the solution after it had passed through successive filters, and found the concentration to be successively smaller. The clarification of barnyard liquor and other colored waters by percolation through fresh clay or loam was mentioned by Sir Humphrey Davy in 1813, by Gazzeri in 1819, Lambuschini in 1830, Browner in 1836, Huxtable in 1848, Bernays in 1849, and by Thompson and Way[a] in 1850. It is especially interesting to note that as early as 1819 Gazzeri considered that loam and clay take up in their pores the soluble matters in solution and retain them to release them by degrees to the plants. In 1830 Lambuschini suggested the name *incorporation* for the fixation of dung liquor by the soil, and in 1836 Browner insisted that soils held back even the soluble salts in dung liquor.

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[a] Bul. No. 50, Bureau of Soils, U. S. Dept. of Agr., 1907.

[b] Bul. No. 28, Bureau of Soils, U. S. Dept. Agr., 1905; Farmers' Bul. No. 257, U. S. Dept. Agr., 1906; Bul. No. 40, Bureau of Soils, U. S. Dept. Agr., 1907.

Liebig found that aqueous ammonia passed through clay lost its odor, and Thompson and Huxtable verified the experiment. In 1850 Way showed that soil likewise absorbed potassium, sodium, calcium, and magnesium, not only from solutions of their hydrates, but of their salts, with both strong and weak acids, the acid remaining in solution unabsorbed and combined with other bases leached from the soil. Phosphoric acid, however, was itself absorbed. Way believed the absorption or replacement of the bases to be total, but Voelcker showed that weak solutions of ammonia could circulate in the soil and still retain some of their ammonia unabsorbed, and Peters[b] demonstrated that however weak the solution used, potassium was never completely absorbed. Frank[c] confirmed Peters's results, using the percolation method. Thus there was introduced the conception of *distribution*, the partition of a soluble substance between solid and liquid, so that no matter how small a quantity of substance be present there is a fraction of it left in solution. And the application of this principle has led to a much better understanding of the retention of soluble material by soils.

Before proceeding to a detailed consideration of the different phenomena of absorption a few precise definitions are in order. The term absorption is used in general to designate the process by which a solid or a liquid draws unto itself and retains within its structure or on its surface another solid, liquid, or gas.

The simplest case of absorption is that of mechanical absorption, or *imbibition*, such as water held by a sponge, by porous solids like brick or charcoal, by powders, including soils, and by bodies which draw liquid or vapor into their most intimate recesses and swell, as, for example, starch with water, or rubber with chloroform.

A second kind of absorption is where a solid retains another solid so that the two form a *homogeneous body* and the mixture is either a

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[a] Storer, Agriculture, 1897, I, pp. 201 and 316; also Jour. Roy. Agr. Soc., **11**, 313 and 366 (1850).

[b] Landw. Vers.-Stat., **2**, 129 (1860).

[c] Ibid., **8**, 45 (1866).

definite chemical compound or a *solid solution.* The criterion of a solid solution is that when present in equilibrium with a liquid solution containing the same components a variation in the percentage of these components in the liquid is accompanied by a corresponding change in the composition of the solid phase. Thus free phosphoric acid added to a soil containing ferric hydroxide is absorbed in such a way that the more P_2O_5 there is in solution the more P_2O_5 is found in the solid ferric hydroxide—that is, the P_2O_5 forms a solid solution with the ferric hydroxide, and its composition changes with that of the liquid solution above it.[a] An even more interesting case is that of the absorption of phosphoric acid by lime. Here the P_2O_5 forms a solid solution with the CaO, the percentage of P_2O_5 in the solid phase increasing with increase of P_2O_5 in the liquid phase until a certain concentration in the liquid is reached, and further increase of P_2O_5 in the liquid causes no increase of P_2O_5 in the solid—that is, a definite compound of CaO and P_2O_5 has been formed.

A special case of absorption has been termed *adsorption,* which may be defined as the existence of a difference in concentration or density of a film adjacent to a bounding solid and the concentration or density of the mass of the liquid or gas which bathes this solid.

Whether this adsorbed film is in a liquid, solid, or gaseous state, or even loosely combined with the solid bounding medium, is not easily determined and has been the subject of much discussion. The change of state from solid to liquid and from liquid to vapor is very gradual. All the recent physical researches, dealing even with hard, polished "solid" surfaces, indicate a mobility of parts, an openness of structure, and a high power of retaining foreign material. But the ability of one body to hold another upon its surface is dependent upon the material of which each consists. So we are accustomed to say that adsorption depends upon the chemical constitution of the solid as well as of the substance adsorbed. Another way of stating the same idea is to attribute adsorption to a specific attraction between solid and adsorbed material.

This preference of one material for another is well shown by the separation of substances in solution from each other by simply percolating the liquid through an absorbent body, which takes one substance from solution, while the other passes into the filtrate. This process has been called *selective absorption* and is of very wide occurrence, although its possibilities as an analytical and technical method of separation are only beginning to be appreciated.

Throughout this paper the terms "solvent," "solute," and "absorbent" are used with the following meanings:

Solvent: A pure liquid used to dissolve some solid, liquid, or gas.

Solute: The substance dissolved by the solvent.

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[a] See Bul. No. 41, Bureau of Soils, U. S. Dept. Agr. The Action of Water and Aqueous Solutions upon Soil Phosphates. Frank K. Cameron and James M. Bell.

Absorbent: The solid body which when placed in a solution abstracts part or all of the dissolved material from the solution.

Further, the terms "gel," "sol," and "colloid" are used with special meanings:

Gel: A number of substances, such as metallic oxides, are precipitated from solutions of their soluble salts as amorphous solids. These solids frequently contain so much of the solvent from which precipitation takes place that they have a jellylike consistency, and consequently the term "gel" has been applied to them. When these gels are formed in an aqueous solution and the liquid held in combination with them is water, they are termed "hydrogels."

Sol: By proper treatment it is possible to cause these gels to redistribute or suspend themselves throughout the liquid from which they were originally precipitated. Such a resuspension of the precipitate in many cases has been found to consist of minute particles of the gel. Where this is the case the opalescent liquid thus formed is termed a "sol." Where the solvent used is water, such a suspension is termed a *hydrosol.*

A *colloid* has been defined as a material which when dissolved will not pass through certain membranes, and has been considered to be of high molecular weight and consequent complexity; a crystalline substance, on the other hand, passes through these membranes. This distinction between colloid and crystalloid is not maintained so rigidly at present, for some crystalline materials show a very slow rate of diffusion through the membranes. At present colloidal solutions are considered to be made up of minute particles in suspension. Consequently, if the absorption of materials from solution by finely divided solids is studied and the relation between this absorption and the formation of these particles into larger aggregates and their consequent settling from suspension, it is found that the general phenomena there observed are parallel to those where the much finer particles of a colloidal solution or precipitated colloid are under consideration.

The referring of various actions otherwise not clear to the presence of "colloidal material" does not now afford that satisfaction which it gave before the intimate relation between colloidal solutions and suspensions of larger particles had been recognized.

In order to bring out clearly the general application of the phenomena of absorption and the general principles derived therefrom, a number of solvents, solutes, and absorbents, in addition to soils and constituents of the soil solution, have been studied. The establishment of these general phenomena in the case of pure substances where no life process enters strengthens very greatly our certainty in their validity when they are found to hold good for such very complex materials as exist in soils and soil solutions.

RÉSUMÉ OF EARLIER WORK.

Hoffman[a] in 1858, summing up the question of removal of nutrient salts from a soil by rains, says:

> It is very probable that each soil possesses a peculiar power of retaining certain nutrient material for plants. But this power appears to have a limit, and whatever material over and above this limit remains in solution, follows the movement of this solution. In this movement of water itself there appears to be a means—at least for certain soils and certain relative positions—of returning to the earth a part of the leached soluble salts. When the rains are not heavy the water in the soil does not penetrate very deeply, and during the evaporation consequent upon hot weather the water from below is again drawn up to the surface and its soluble salts are returned to the fine soil grains.

In 1866 Frank[b] investigated the absorption of potassium chloride by soil. He used cylinders 3 inches in diameter and 3 to 6 feet long. The soil was carefully removed from the field and placed in these cylinders, keeping the same relative position of the soil layers. Distilled water was passed till only a trace of chlorine came through, as shown by a slight turbidity when silver nitrate was added. Then he placed 4 liters of potassium chloride solution, 1 gram per liter (0.1 per cent), in a flask and inverted it above the soil, so that the liquid might percolate under atmospheric pressure alone as the soil took it up, as illustrated in figure 1. He found that the salt solution drove out the water which remained in the soil, no diffusing of one liquid into the other being noticed. After he had made sure that the soil contained only salt solution, by analyzing the liquid which drained from tap No. 2, 12 inches below the surface of the soil, and finding that the same per cent of chlorine was in this liquid as in the original solution, he analyzed another portion of this same percolate and found that it contained only 9 per cent of its original potassium, 91 per cent being retained by 12 inches of soil. A similar test of the percolate from tap 3, 18 inches below the surface, showed 4.5 per cent of potassium left and 95.5 per cent absorbed. The taps lower down (4, 5, 6, etc.,) showed little further decrease in the potassium in the percolates, and even after the solution had passed through 6 feet of soil it always retained 2 to 2.5 per cent of its original potassium. So there appears to be a certain dilution of the solution—in this case 1 part in 40,000 to 50,000 parts—at which water is more effective in holding the dissolved material than the absorbing power of the soil.

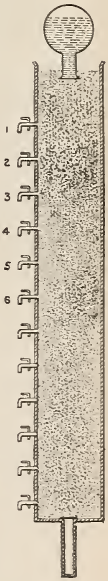

FIG. 1.—Percolation tube used by Frank in his studies on absorption.

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[a] Jahresb. Agr.-Chem., **1**, 16 (1858); see also Liebig, Ann. Chem. u. Pharm., **105**, 109 (1858); Grouven, Agron. Zeitung, 1858, p. 1; also Jahresb. Agr.-Chem., **1**, 14 (1858); Babos, Landw. Ber. v. B. (1858), p. 1.

[b] Landw. Vers.-Stat., **8**, 45 (1866).

Potassium is still more quickly absorbed from a solution of potassium sulphate, so that with a potassium sulphate solution it will not penetrate the soil so deeply as with a potassium chloride solution.

Frank found on using a solution of 1 gram pure potassium chloride and 1 gram sodium chloride to 100 parts of water that the potassium content of the percolate through 18 inches of soil still contained 18 per cent of its original potassium, as against 5 per cent (average) when no sodium chloride was present. Likewise, after passing through 4 feet of soil the percolate gave 5 per cent of the original potassium content, whereas with no sodium chloride in solution the potassium content was reduced to some 3 per cent of that in the solution added. Thus the presence of sodium chloride lowers the absorption of potassium and carries it deeper into the soil. In addition, a cylinder of earth which had been allowed to absorb potassium from a pure potassium chloride solution was percolated with distilled water till the runnings showed no potassium in solution. Then a solution of sodium chloride was passed through and potassium immediately appeared in the percolates. Frank was not at all sure that this points to a chemical substitution of potassium by sodium.

He found that the chlorine was absorbed from a sodium chloride solution percolated through earth and that most of the chlorine in the percolates was combined with sodium. It appeared to him, accordingly, that sodium chloride is not so easily decomposed by the earth as potassium chloride, and that a part of the sodium chloride is absorbed unchanged. Long-continued washing with pure water removed almost all the sodium chloride, while, as already stated, this can not be done in the case of potassium.

Next he tried the effect of sodium chloride upon the most insoluble phosphates in the soil. The upper 3 inches of soil in a cylinder filled with earth (as above described) was mixed with precipitated well-washed basic calcium phosphate and the cylinder percolated with distilled water. The filtration through these cylinders—4 to 6 feet long—took four weeks. At 12 inches below the surface only traces of phosphoric acid could be detected in the percolate; but, on the contrary, when sodium chloride solution (1 gram per liter) was passed through the soil phosphates were detected as far down in the cylinder as 4 feet and below.

Salomon[a] gives the absorption of calcium by various soils and soil constituents from several concentrations of calcium nitrate solution, to which was added sufficient ammonia to neutralize exactly the nitric acid of the calcium nitrate. The solution was placed with the soil in a flask, shaken, and allowed to stand forty-eight hours, filtered and analyzed and the absorbed calcium determined by difference. The results are given in Table I.

---

[a] Landw. Vers.-Stat., 9, 351 (1867).

Table I.—*Absorption of calcium from amoniacal calcium nitrate solution by soils, according to Salomon.*

		Used in experiment.		CaO in 200 c.c. solution added.	CaO remaining in 200 c.c. of solution.	CaO absorbed by 100 grams soil.
		Soil.	Solution.			
		Grams.	*C.c.*	*Grams.*	*Gram.*	*Gram.*
1	Soil from Möckern	100	200	0.1	0.0788	0.0212
2	do	100	200	.2	.1580	.0420
3	do	100	200	.4	.3096	.0904
4	do	50	100	1.0	.8120	.1880
5	Russian black earth	100	200	.1	.0848	.0152
6	do	100	200	.2	.1580	.0420
7	do	50	100	.4	.2344	.1656
8	do	50	100	1.0	.5960	.4040
9	White "Kujawischer"	50	100	.2	.1292	.0708
10	do	50	100	.4	.2701	.1299
11	do	50	100	1.0	.8586	.1414
12	Black "Kujawischer"	25	50	.2	.1071	.0929
13	do	25	50	.5	.2862	.2138
14	do	25	50	1.0	.6979	.3021
15	Kaolin from Salzmunde	50	100	.2	.1743	.0257
16	do	50	100	.5	.4306	.0694
17	do	50	100	1.0	.8619	.1381
18	Tile clay	50	100	.2	.1704	.0296
19	do	50	100	.5	.3500	.1500
20	do	50	100	1.0	.7326	.2674
21	Ferric hydroxide	25	50	.2	.0490	.1510
22	do	25	50	1.0	.0576	.9424
23	Aluminum hydroxide	50	100	.2	.0000	.2000
24	do	25	50	.5	.0226	.4774
25	do	25	50	1.0	.309	.9691
26	Silicic acid (hydrated)	50	100	.2	.0659	.1341
27	do	50	100	.5	.1664	.3335
28	do	50	100	1.0	.2388	.7612
29	Kaolin+aluminum hydroxide, equal parts	50	100	.4	.0106	.3894
30	100 grams kaolin+25 grams ferric hydroxide	125	200	1.0	.3480	.6520
31	50 grams kaolin+50 grams ferric hydroxide	100	200	1.0	.0435	.9565
32	Soil from Möckern	50	200	1.0	.8772	[a].1228
33	Russian black earth	50	200	.5	.2184	[a].2816

[a] Effect of mass of earth used.

The behavior of the Russian black earth, which contains 9 to 15 per cent of humus, compared with those soils poor in humus, shows that the humus in the Russian black earth must be already saturated with bases. Salomon's predecessor, Pochwistneff, had already found by direct investigation that this is the case and that the black earth contains calcium humate. The soil from Möckern shows a lower absorption than the black earth for a solution containing 0.5 gram calcium oxide per liter, and both soils show the same degree of absorption for a 1-gram calcium oxide per liter solution. The other soils, as, for example, the white "Kujawischer" soil, which contains hardly a trace of humus, nevertheless show an absorption for calcium nearly equal to that of humus-rich soils, such as the black "Kujawischer" and the Russian black earth.

The similarity between the Russian black earth and the tile clay—in that both show a change in absorption with increasing concentration—suggests that the cause can not be in the humus content of the black earth. Salomon considers that such a calcium solution as was used would probably not act upon humic acid which had been already saturated with bases and would probably be changed only where free humic acid, or humic acid dissolved in carbon dioxide and alkalies, is present.

It is evident that all the solute is not withdrawn from the solutions even at low concentrations; apparently the aluminum hydroxide absorbs all the calcium from a 0.1 per cent solution, but this exception to the general rule was doubtless due to the presence of ammonium carbonate in the alumina, which precipitated the calcium as carbonate. The aluminum hydroxide was prepared from aluminum sulphate by ammonia and washed with ammonium chloride.

The white "Kujawischer" soil (entirely free from calcium) absorbed almost the same mass of calcium from a 0.2 per cent solution as from a 0.5 per cent solution. This means that the absorption capacity is limited. The black "Kujawischer" soil shows a similar tendency toward an absorption limit.

Biedermann [a] prefaces a research on absorption as follows:

> Since it has been made clear that of itself the chemical analysis of a soil can give no indication as to its value in respect to cultivation and crop yield, one is forced to study the properties of the soil in other ways, and thus it is soon discovered that the absorptive power of the soil for soluble fertilizers—the ability to fix the same and then to give them up to the plants—is of great significance for practical agriculture as well as for the interesting philosophical question, In what form do the plants obtain their nourishment from the soil?

Biedermann studied the absorption of potassium and of phosphates by soils, and he showed the magnitude of the absorption effect for a number of soils. He concludes that chalk, magnesia, and sulphuric acid do not affect absorption by the soil, and suggests that by use of a suitable solute the absorptive power of a soil may be determined—possibly by potassium phosphate. He tried potassium carbonate solution, percolating it through different soils and titrating the liquid passed through with sulphuric acid, but the results were unsatisfactory.

The quantities of potassium absorbed by different soils vary considerably, and it is certain that the magnitude of absorption is in accord with the value of a soil, although neither the quantity of bases extracted from the soil by means of ammonium tartrate-oxalate solution, nor the ferric hydroxide or aluminum hydroxide content of the soil, nor the quantity of humus in the soil—as shown by weight loss on ignition—give a certain indication of the soil's productive power.

Treutler [b] in a series of researches has studied the absorption and resolution of potassium by soils as affected by other fertilizer agencies. In all his work he used cylinders 9.7 cm. wide and 90 cm. long. Into each cylinder was shaken 4 pounds of earth (containing 85.5 per cent of fine earth), and then 0.5 pound of earth was rubbed up with the potassium salt and with the fertilizer, whose effect upon the absorption of potassium it was desired to study. The 4.5 pounds of earth had a depth of 29 cm. in the cylinder. In each experiment the earth was weighed air dry. The quantity of potassium salt was so chosen that exactly 1 gram of potassium oxide was added to the 4.5 pounds of earth. For comparison blank experiments were made, using each potassium salt alone and the cylinder then percolated with distilled water to ascertain the per cent of potassium the earth would absorb. The 4.5-pound portion of soil required 672 cm. of water to saturate it, so that in each experiment 1,672 c. c. of water were passed through the soil in order to obtain a liter of percolate. This same percolate was repassed through the soil 12 times in order to obtain the equilibrium conditions. Table II is compiled from Treutler's results:

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[a] Landw. Vers.-Stat., **11**, 1, (1869).

[b] Landw. Vers.-Stat., **12**, 184 (1869): **15**, 371 (1872).

Table II.—*Effect of various fertilizers upon the absorption of potassium by a soil, compiled from the results of Treutler.*

[Four and one-half pounds of earth 29 centimeters deep, percolated 12 times with the same percolate, 1,672 cubic centimeters in volume, to insure equilibrium.]

Fertilizer added in top 0.5 pound of soil.	Potassium absorbed.			
	1.849 grams K_2SO_4 added.	2.146 grams KNO_3 added.	1.583 grams KCl added.	1.467 grams K_2CO_3 added.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Bone dust, 500 grams	45.3	54,43	58.0	51,52
Bone dust, 50 grams	81.6	95.09	79.8	98.00
Humus soil, 250 grams	83.4	95.12	80.7	98.13
Cow manure, 80 grams	89.7	92.21	82.2	97.00
Sheep manure, 80 grams	93.2	89.74	90.5	90.31
Horse manure, 80 grams	93.0	93.62	91.3	85.63
Cow urine, 125 grams	96.3	90.68	91.5	94.99
Chili saltpeter, 20 grams	86.3	86.83	....	83.75
Ammonium carbonate, 20 grams	88.7	89.61	85.0	88.37
Superphosphate, 20 grams	89.6	87.90	86.1	91.98
Magnesium sulphate, 5 grams	90.2	83.52	....	96.76
Gypsum, 20 grams	90.4	90.01	88.6	93.05
Humus soil, 250 grams + $(NH_4)x(CO_3)y$, 20 grams	91.8	82.25	88.7	94.65
Water containing carbon dioxide, 1 liter	93.7	94.96	92.9	95.62
Potassium magnesium sulphate, 3.698 grams	93.9	84.29	....	89.07
Sodium chloride, 10 grams	96.4	90.90	95.4	[a] 100.00
Distilled water alone passed through soil	[b] 97.9	[a] 91.75	[b] 94.7	[a] 97.60

[a] Landw. Vers.-Stat., **15**, 372 (1872).

[b] Landw. Vers.-Stat., **12**, 191 (1869).

Treutler found that the greatest quantity of potassium was absorbed from the sulphate, the carbonate, chloride, and nitrate following in the order named, and he concluded, therefore, that a deeper penetration of potassium into the soil was secured by the use of potassium chloride than by the use of potassium sulphate as a fertilizer. He found, further, that the relative absorption from these two salts was not materially affected by the addition of other salts and of the common fertilizers. The absorption of the potassium from the carbonate and nitrate is more affected by other agencies than is the absorption from the sulphate or from the chloride, the absorption from the carbonate being affected to the greatest extent.

In general, the addition of other mineral salts depressed the absorption of potassium, a marked influence being noticed in the case of sodium chloride, which further brought into solution in the soil percolate noticeable quantities of magnesium salt; and for this reason Treutler concludes that sodium chloride is harmful rather than beneficial as a fertilizer.

Bone dust and superphosphate depress the absorption of potassium; and Treutler considers them especially useful on this account, as they tend to increase the concentration of potassium salts as well as of phosphoric acid and ammonia in the soil solutions. Gypsum and magnesium sulphate were found to increase the concentration of potassium in the percolate. Humus, and especially humus mixed with ammonium carbonate, appeared to decrease the absorption, which effect is attributed to the formation of large quantities of carbon dioxide from the humus.

Knop[a] includes under absorption the process of conversion of a solid first to soluble form and then the spreading of the substance upon the soil grains in such a way as to withdraw it from solution, regardless of whether chemical affinity or surface attraction is the cause of this retention or whether the substance absorbed is decomposed chemically or absorbed unchanged. He used a solution of 1 gram ammonium chloride in 208 c. c. of water to determine the absorptive power of a soil. One hundred grams of earth were taken for analysis. The nitrogen corresponding to the ammonia still left in solution was determined and the number of cubic centimeters of nitrogen absorbed by the soil taken as the measure of the absorptive power of the soil. Using this method, he found the absorption of ammonia by 38 soils which had been analyzed chemically.

In a few cases he compared the absorption of potassium with that of ammonia. For this purpose he employed an analytical procedure which has since been followed by a number of investigators. These two analytical methods for ammonia and for potassium are given in detail here, since a number of investigators have used them to express their data on the absorption by soils in terms of Knop's absorption figure, i. e., the cubic centimeters of nitrogen (as ammonia) absorbed by 100 grams of soil, from 200 c. c. of the ammonium chloride solution described above. A potassium carbonate solution was taken of such concentration that 100 c. c. contained exactly the weight of potassium equivalent to 100 c. c. of nitrogen gas. Fifty cubic centimeters of this solution plus 50 c. c. of the above ammonium chloride solution when evaporated to dryness gave all the potassium as chloride, the ammonia and carbon dioxide going off upon ignition. But when one adds 100 c. c. of the ammonium chloride solution to 50 c. c. of this potassium carbonate solution and evaporates to dryness there remains sufficient ammonium chloride to give by the nitrometer method 50 c. c. of nitrogen. This fact was made the basis for a quantitative estimation of the potassium by adding ammonium chloride to the potassium carbonate solution, evaporating, and then determining the nitrogen in the residue.

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[a] Knop's book, Die Bonitirung der Ackererde, published by H. Haessel, Leipzig, 1872, 2d edition, is not generally available. We are indebted to the Massachusetts State Experiment Station, Amherst, for the use of their copy.

Knop believed that the absorptive power of a soil was proportional to the "Aufgeschlossene Silicatbasen," i. e., such substances as ferric oxide, alumina, etc. His data, on the whole, seems to bear out this conclusion. But later investigators[a] have shown that this is by no means the sole factor to be considered; and, indeed, Knop himself admitted this. He found the absorption for one and the same soil a constant, but seems to have no clear idea of the effect of end concentration of solution upon the quantity of solute absorbed. While he recognizes that substances in a soil capable of forming well-defined chemical compounds will of course absorb from a solution the material with which they can combine, he still observes phenomena in the absorption of potassium and of ammonia which he can not explain in the ordinary chemical way. He thinks the absorption of phosphoric acid may be explained as due to chemical combination, and if it were merely a question of the absorption of caustic potash or of ammonium hydroxide he would class these also as reacting chemically with the soil. But he finds that the selective absorption—the separation of these bases from the strongest acids by soil—and the effects upon absorption produced by varying quantities of soil, of solvent, and of solute all complicate the problem so much that he can not give a simple chemical explanation of it. He shows, too, that the power of a soil to absorb moisture from the air parallels in general its absorption of ammonia from ammonium chloride solution.

Frey[b] continued the work of Knop and confirmed his results.

Pillitz[c] showed that soils possess a saturation point for ammonia absorbed from ammonium chloride solution, and Fesca[d] recognized the influence of extent of soil grain surface in determining the absorption capacity. In 1887 Kellner[e] confirmed Pillitz's experiments and from new work concludes that ammonia and potassium are absorbed in chemically equivalent quantities by soils. Kellner extracts absorbed potassium from a soil thus: The soil (20 grams) is heated with 50 c. c. saturated ammonium chloride solution for a half hour, the solution poured off, the soil washed with hot distilled water, and fresh ammonium chloride solution added to the soil. This extraction is repeated (fifteen to twenty times) until the filtered solution leaves no solid residue upon evaporation and ignition. In this manner he recovers slightly more potassium than the soil had taken up from a known potassium chloride solution. This recovery is especially interesting since Way[a] and Eichorn, Dietrich,[b] Peters,[c] and Schuhmacher[d] were all unable to substitute completely one absorbed base by another. This method of substitution used by Kellner is essentially a percolation, and recognizes in a practical way the distribution of potassium between soil and solution. He also suggests that absorbed potassium may be more firmly fixed in an insoluble form, as, for instance, by internal arrangement of the double silicates containing water.[e] He further concludes that for potassium and calcium it may be considered as settled that these elements can afford nourishment to plants only when in dissolved or in absorbed condition.

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[a] See Sachsse, Lehrbuch der Agrikulturchemie, p. 169. "Mehr als eine gans grobe Annäherung an ein Verhältniss zwischen aufgeschlossenen Silikatbasen und Absorption lässt sich nicht erwarten."

[b] Landw. Vers.-Stat., **18**, 3 (1875).

[c] Zeit. anal. Chem., **14**, 55, 285 (1875).

[d] Die agronomische Bodenuntersuchung und Kartirung, 1879, p. 28.

[e] Landw. Vers.-Stat., **33**, 359 (1887).

Fiedler[f] has investigated the effect of sodium nitrate upon the absorption of phosphoric acid and potassium by soils. He concludes that the sodium nitrate prevents the percolating soil moisture from carrying phosphoric acid down with it to lower levels. On the other hand, potassium is less absorbed in the presence of the sodium nitrate and is carried deeper into the earth. When calcium is present in the soil in goodly quantity, this effect of sodium nitrate upon the potassium is not observed, while the sodium nitrate still is able to act upon the phosphate to prevent its removal by leaching. Fiedler suggests that as the quantity of sodium nitrate is increased more calcium nitrate is formed, and that this precipitates the phosphoric acid of the soluble phosphates as insoluble calcium phosphate.

Van Bemmelen,[g] in 1888, sums up the results of an extended research upon the absorption of soluble material from solution by soils and soil constituents as follows:

> Absorption compounds are formed from their components according to inconstant molecular ratios. They must be distinguished from chemical compounds, although they may often be rearranged into definite chemical individuals. Colloidal substances form such absorption compounds with water or other liquids, and with bases, acids, and salts when in contact with their solutions. The absorptive power of a colloid depends upon its molecular state of aggregation, and is also different for the different

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[a] Jour. Roy. Agr. Soc., **11**, 313 (1850).

[b] Jahresb. Agr. Chem., **1**, 29 (1858); **5**, 12 (1862).

[c] Ibid., **3**, 11 (1860).

[d] Ibid., **10**, 21 (1867).

[e] Landw. Vers.-Stat., **33**, 364 (1887).

[f] Landw. Vers.-Stat., **26**, 135 (1881).

[g] Landw. Vers.-Stat., **35**, 136 (1888).

substances which it absorbs. The power of absorption decreases as the colloid holds absorbed more and more of the substance. The relation between the concentration in the colloid and the concentration in the solution at equilibrium is a complex function (still unknown) of these concentrations and of the temperature. The absorbed substances may be substituted by other substances absorbed from solution by the colloid; bases may in this manner be substituted for the bases of a salt solution. Colloids may often produce chemical decomposition of salts by their power of absorption. The soil contains colloids, colloidal silicates, iron oxide, silicic acid, and humus substances, all of which may bring about these actions.

Van Bemmelen thinks that the absorptive power of a soil is mainly to be ascribed to the colloidal oxides and silicates present in it.

Humus substances are decomposition and degradation products of carbohydrates, albuminoids, etc. Humus will absorb ammonia and organic materials to a greater or less degree. Natural humus contains nitrogen, of which a part may be driven off as ammonia by dilute potassium hydroxide; on treating further with strong potash solution ammonia is unmistakably given off anew. He states that when peat is analyzed it shows the presence of alkali bases, which for the most part must be absorbed, since the peat is lacking in mineral acids sufficient to neutralize them.

Consideration of the solubility of the humus substances shows that some exist which are of themselves soluble in water. Some, indeed, according to Van Bemmelen, may go through colloidal membranes on dialyzing, but for the most part their solubility is a colloidal solubility. They form generally opalescent liquids when they are dissolved. Frequently the solubility depends upon small masses of alkali or of ammonia. Often the humus constituents may be separated by the influence of a small mass of acid or salt or by drying, as well as in other ways changed into an insoluble modification—as is true for colloidal substances in general.

Many dissolved humus substances show the properties of a hydrogel. The substance when dissolved by an alkali and coagulated by an acid after washing out partly dissolves again, and this solution is of a colloidal nature. These humus substances form absorption complexes with acids and salts, but most easily with bases. The dissolved humus substances form with alkalies soluble complexes which may be separated by alcohol.

Heiden[a] found that peat and various preparations of the supposed humic acids when brought into solutions of chloride of potassium and chloride of ammonium remove a portion of these salts from the liquid, leaving the solutions perceptibly weaker. The removed salts were for the most part readily recovered by a small quantity of water. Schumacher[b] observed that humus artificially prepared by the action of oil of vitriol on sugar when placed in 10 times its quantity of solutions of various salts containing about 0.5 per cent of solid matter absorbed of sulphates of soda and ammonium and of chlorides of calcium and ammonium about 2 per cent, of sulphate of potash 4 per cent, and of phosphate of soda 10 per cent. Schumacher also noticed that sulphate of potash is able to expel sulphate of ammonium from so-called humic acid which has been saturated with the latter salt, but that the latter can not displace the former. In Schumacher's experiments pure water freely dissolved the salts absorbed by the supposed humic acid.[a]

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[a] Hoffmann's Jahresb., 1866, p. 29.

[b] Hoffmann's Jahresb., 1867, p. 18.

A neat experimental demonstration of the absorption of soluble material from solution was given in 1867. Humus and a weak solution of oxalic acid were placed in a beaker.[b] The humus absorbed the oxalic acid from solution, and after the humus had settled and the supernatant solution had become clear a little sack made of collodion, attached to a glass tube and filled with water and calcium carbonate, was suspended in the solution, not touching the layer of settled-out humus. The oxalic acid of the solution diffused into the collodion sack and reacted with the calcium carbonate to form insoluble calcium oxalate. Thus the concentration of the solution in oxalic acid is lowered and the absorbed oxalic acid from the humus comes again into solution, and finally the absorbed oxalic acid is practically all removed from the humus. This was shown by removing the humus and extracting with hot water. The filtrate showed no trace of oxalic acid. The humus was free from bases, so that a chemical combination could not have been formed. If the humus had been in contact with a nutrient solution, and had absorbed plant food from it, a plant whose roots were in the solution would have behaved in a similar manner, absorbing the soluble matter from solution just as did the collodion sack containing calcium carbonate.

From calcium phosphate, humus suspended in water can absorb calcium and considerable free phosphoric acid.

That plant substances and animal tissues may absorb inorganic chemical compounds accompanied even by chemical decomposition of inorganic solute is known. Consequently one may expect of the humus constituents that they are in condition to absorb whole salts and acids in small amounts. If these humus constituents are coagulated from aqueous solution by a small mass of acid or salt, they are very difficult to free of acids or salts by washing. This fact van Bemmelen considers as showing that the acid or the salt is absorbed by a colloid.[c]

According to van Bemmelen, compounds of the so-called humic acid soluble in water are obtained when the aqueous or alkaline solution of a humus substance is treated with a solution of the hydrates of the alkaline earths or salts of the alkaline earths and metallic oxides—for instance, calcium, lead, and iron, etc. These compounds are also of colloidal nature and of changing composition. The humus substance in aqueous solution is coagulated and precipitated by a small mass of salt, and may fix a certain mass of base by absorption. Even an undissolved base in a hydrogel condition may precipitate humic acid, as, for instance, the hydrogel of alumina.

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[a] Hoffmann's Jahresb., 1867, p. 18. See also Johnson, How Crops Feed, p. 172.

[b] Quoted by Schumacher, Physik der Pflanze, p. 304, Berlin, 1867.

[c] Van Bemmelen, Landw. Vers.-Stat., **35**, 69 (1888).

The humus substances hold the potassium more strongly combined than the calcium, but the calcium compound is less soluble. If, therefore, humus is treated with a solution of a potassium salt, a certain mass of potassium is fixed, along with an interchange with calcium and magnesium; and if the soluble compound of humus is treated with an alkali or calcium solution, then it will form an insoluble calcium humus compound. The action of humus substances upon alkali carbonates, alkali phosphates, and, in general, salts of weak acids, is such that certain masses of alkali are absorbed with exchange for calcium and magnesium. In addition, alkali is absorbed by the insoluble humus substances, humus substance is brought into solution by the alkali thus set free, and the above mineral acids are precipitated by alkaline earths. Since, in general, the absorption of base is greater than of acid, the remaining solution has an acid reaction, although the salt was one of a strong base with a weak acid.

The decolorizing action of wood charcoal was discovered in 1791 by Lowitz,[a] and later Figuier showed the greater absorbing power of animal charcoal. Payen[b] found that charcoal could absorb lime from solution as well as coloring matter. Graham[c] ascribed this decolorization to the concentration of coloring matter upon the surface of the carbon—that is, to adsorption—a purely mechanical explanation. He found that charcoal also acts chemically upon solutions, extracting the metal from solutions. Weppen[d] found that one salt affects the absorption of another by charcoal. Birnbaum and Bombasch[e] found that boneblack absorbs a small amount of ammonia from ammonium salts and that in other cases the acid and basic radicals are absorbed, but not in equivalent proportions. Qualitative experiments by Liebermann[f] have shown that the acidity or basicity of a solution treated with charcoal changes as well as the concentration. Similar results have been obtained by Moride,[g]

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[a] See Ostwald, Stoechiometrie, 1891, p. 1093.

[b] Ann. Chim. Phys., **21**, 215 (1822).

[c] Quarterly Jour. Sci. (new series), **7**, 120 (1830); also Pogg. Ann., **19**, 139 (1830).

[d] Ann. Phys. Chem., **55**, 241 (1845); **59**, 354 (1846).

[e] Dingl. Poly. Jour., **218**, 148 (1876).

[f] Wien. Akad. Ber., **74**, 331 (1877).

[g] Compt. rend., **41**, 605 (1855).

Esprit,[a] and Heintz,[b] and Kelberin [c] has studied the absorption of hydrochloric acid by charcoal. Kroeker [d] and Lagergren [e] have used charcoal in studying the distribution of the solute between the solvent and absorbent, and the latter investigator used charcoal in studying the rate of absorption. Oechsner de Coninck[f] has shown that heavy metals are removed from solution of their salts by charcoal.

Rosenthaler and Türk[g] have studied the absorption of various pharmaceutical substances from their solutions when treated under standard conditions with different kinds of charcoal. These charcoals may be divided, according to their absorbent powers, into strongly absorbent—bone, flesh, and "vegetable blood" charcoals, in the order named—and weakly absorbent or nonabsorbent—blood, lime-wood, and spongy charcoals. For the same kind of charcoal the absorption of any substance varies with the solvent which is employed. The absorption is by far the strongest in aqueous solutions; it is less with ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and least of all with chloroform solutions. The speed of absorption depends on the same factors as influence the amount of absorption, being greatest in the case of bone charcoal and aqueous solutions. The quantity of substance absorbed by a given quantity of charcoal is relatively less for concentrated solutions than for dilute solutions. All the circumstances which favor absorption act in a similar degree in resisting the reextraction of the absorbed substance. The decolorizing power of the charcoal is dependent on its absorbing power. As regards the use of charcoal for decolorizing purposes, the authors state that the charcoal must be carefully purified before use, either by repeated extraction with the solvent which is to be used or by igniting gently and washing with acid. The quantity of charcoal employed should be as small as possible. It is not necessary to heat the liquid with the charcoal; several hours' contact at the ordinary temperature will suffice. The decolorization should not, for preference, be effected in an aqueous solution, because the loss of substance by absorption is at a maximum with that solvent; the solution should be as concentrated as possible. Easily oxidizable substances should not be decolorized by animal charcoal, because this charcoal has a powerful oxidizing action; the oxidation of alkaloids is retarded by treating them in the form of salts. Blood charcoal has the strongest oxidizing action, lime-wood charcoal has hardly any. Bone and flesh charcoals can be employed in the determination of caffeine without loss of alkaloid, but in the determination of sugars, etc., in wine and other liquids charcoal should not be used unless it has been proved that no loss by absorption takes place under the conditions of the experiment. The close interdependence of the decolorizing and absorbent properties of charcoals suggests that the decolorization is due to absorption of the coloring matters. The fact that successful results can be obtained in practice depends, first, on the circumstance that the amount of coloring matter is generally only a fraction of the total substance in solution, and, second, on a selective absorption, according to which the quantity absorbed is generally proportional to the molecular weight, most coloring matters being substances of high molecular weight.

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[a] Jour. pharm., **16**, 192 (1849).

[b] Lieb. Ann., **187**, 223 (1877).

[c] See Ostwald, Lehrbuch der Allgemeine Chemie (1891) p. 1096.

[d] Uber die Adsorption gelöster Körper durch Kohle, Diss. Berlin, 1892.

[e] Bihang till K. Sv. Vet. Akad. Handl., **24**, Afd. II, No. 4 (1898).

[f] Compt. rend., **130**, 1627 (1900).

[g] Arch. Pharm., **244**, 517 (1906).

The experiments of Kellner[a] show that platinum black absorbs minute quantities of acids and alkalies, but gives them up to water on standing.

Many rock powders possess the power of absorbing the coloring matter from solutions in which the powders are suspended. The alkalinity of water in which rock powders have been in suspension has been shown in a large number of cases by Clarke.[b] Some powders, such as very finely powdered orthoclase, have been found to show no red color with phenolphthalein. This is due to the absorption of the color by the powder. A suspension of orthoclase in water which showed no color on the addition of phenolphthalein was allowed to settle, and the supernatant solution after being poured off showed a distinct red color with a further addition of phenolphthalein. When a little of the suspended material was added to the solution again the red color disappeared from the solutions, but was seen on the surface of the solid particles. The test of alkalinity of a solution by phenolphthalein can not properly be made if there are present in suspension finely divided particles which have the power of absorbing the indicator. Another substance which absorbs the phenolphthalein is magnesium ammonium phosphate.

Hulett and Duschak[c] have investigated the nature of barium sulphate precipitates, which are nearly always found to weigh too much, and attribute the results observed by them to the formation of a compound $BaCl.HSO_4$. On long standing or heating of the precipitate hydrochloric acid was given off—which is in harmony with the assumption that hydrochloric acid was absorbed on the surface of the precipitate and escaped when the area of surface was reduced. Barium sulphate precipitates have been found to absorb many compounds from solution. Vanino and Hartl[a] observed that this precipitate absorbs colloidal metals from solution, and Patten[b] observed that salts of nickel, cobalt, chromium, iron, and manganese in solution are absorbed by barium sulphate precipitates. Korte[c] has found that not only does barium sulphate absorb salts from solution, but also calcium oxalate precipitates absorb magnesium oxalate, even in the presence of ammonium chloride, and ferric hydroxide absorbs manganese hydroxide and nickel hydroxide. Ostwald[d] has called attention to similar cases.

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[a] Ann. Phys. Chem., **57**, 79 (1895).

[b] Bul. No. 167, U. S. Geol. Survey, p. 156 (1900).

[c] Zeit. anorg. Chem., **40**, 196 (1904). See also Trans. Am. Electro-Chem. Soc., **12**, 257 (1908).

Suida[e] has shown that the fixation of dyes by animal textiles (wool or silk) is due in part to the amphoteric character of the amino acids which enter into the composition of these albuminoid bodies. He has separated bodies from these complex albuminoid fibers which, like the original substance, fix acid or basic dyes, since these simpler decomposition products are themselves amino acids, $R(NH_2)(COOH)$.

Colloidal substances have the power of absorption to a very marked degree. In numerous papers[f] van Bemmelen has shown that all colloids absorb organic and inorganic compounds. They have the power of absorbing one of the constituents of an inorganic salt, leaving the solution acid or alkaline, as the case may be. The distribution of the absorbed material between water and the colloid is not constant, but depends upon the concentration of the solution.

The use of clays as absorbents has been specially valuable in technical processes, and more especially in the clarification and separation of oils. The technical literature on this subject is now enormous, but, while of the highest importance for certain commercial processes, the work which has been done adds comparatively little to our theoretical knowledge of the subject, and hence is not given in detail.

SELECTIVE ABSORPTION.

It has been found by numerous investigators that when an absorbent is brought into contact with a solution containing two or more solutes these solutes may be absorbed in very different degrees, and thus more or less complete separation of the solutes may be effected. A particularly interesting case of selective absorption is where a substance like a salt is separated into its constituent parts and either the acid or the base from which the salt is derived is absorbed to a greater extent, leaving the solution more concentrated with respect to the least-absorbed constituent. Thus, for instance, a solution of potassium chloride agitated in contact with a soil, or cotton, or carbon black, or similar materials which do not themselves react with either the base or the acid, nevertheless leaves a solution which is markedly acid. This phenomenon is particularly marked in the case of such salts as are greatly hydrolyzed when brought into contact with water.

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[a] Ber., **37**, 3620 (1904).

[b] Jour. Am. Chem. Soc., **25**, 186 (1903).

[c] Jour. Chem. Soc., **87**, 1503 (1905).

[d] Foundations of Analytical Chemistry, Trans. by McGowan, 1895, p. 26.

[e] Monatsh. Chem., **25**, 1107 (1904); **26**, 413, 855 (1905); **27**, 225 (1906); Hoppe-Seyler's Zeit. physiol. Chem., **5**, 174 (1906); C. f. the literature on dyes and amino acids given there.

[f] Landw. Vers.-Stat., **35**, 72 (1888); Jour. prakt. Chem., **23** , 324 (1881); Zeit. phys. Chem., **18**, 331 (1895); Zeit. anorg. Chem., **13**, 233 (1896); **18**, 14, 98 (1898); **23**, 111, 321 (1900); **30**, 265 (1902); **35**, 23, 338 (1904); Arch. Néer. (2), **6**, 607 (1903).

A third type of selective absorption has been observed in a few cases and designated as negative absorption—that is, there is an increase in the concentration of the solute after contact with the absorbent. This is obviously due to the fact that the solvent is taken up or absorbed to a relatively greater extent than the solute. This perhaps theoretically should not be considered as a special case, since we are yet without criteria to distinguish between solvent and solute, and it is rather a matter of convenience to consider the material in excess as the solvent.

CARBON.

SEPARATION OF SILVER FROM SILVER NITRATE.

Graham[a] studied a number of interesting cases of selective absorption. He found, for instance, that when a solution of silver nitrate was passed through powdered charcoal a separation of the salt was effected, and a subsequent examination of the charcoal disclosed the presence of metallic silver in small spangles.

EXTRACTION OF METALS FROM NEUTRAL SALT SOLUTIONS.

Esprit,[b] Moride,[c] and Heintz[d] obtained similar selective absorptions with carbon, the metal being extracted from its neutral salt solution and the resulting solution having in consequence an acid reaction.

Oechsner de Coninck[e] effected separations of the heavy metals from their solutions by percolating through charcoal. In this way iron could be quantitatively separated from solutions of its chloride.

LIBERATION OF ACID FROM NEUTRAL SALT SOLUTIONS.

Liebermann[f] found that the following salt solutions passed through animal charcoal yielded acid solutions, some of which on distillation gave the free acid: The barium salt of the acid formed by oxidizing glycerin with chromic acid, barium formate, sodium acetate, lead acetate, calcium glycollate, zinc lactate, ammonium oxalate, sodium-potassium tartrate, sodium borate (previously alkaline), trisodium phosphate (previously very alkaline), disodium phosphate, ferrous sulphate, copper sulphate, silver nitrate, and potassium acetate. The following aqueous salt solutions, however, showed no change of alkalinity or acidity, but the concentrations were less after passing through carbon: Sodium chloride, nitrate, and sulphate; potassium chloride, iodide, bromide, cyanide, sulphocyanate, and sulphate; calcium chloride, and barium chloride and nitrate. In the case of morphine acetate and caffein citrate, the first percolates contained none of the solute, but after a time the free acids came through.

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[a] Pogg. Ann., **19**, 139 (1830).

[b] Jour. Pharm., **16**, 192 (1849).

[c] Compt. rend., **41**, 605 (1855).

[d] Lieb. Ann., **187**, 227 (1877).

[e] Compt. rend., **130**, 1627 (1900).

[f] Wien. Akad. Ber., **74**, 331 (1877).

SEPARATION OF ORGANIC DYES INTO ACID AND BASIC CONSTITUENTS.

Freundlich and Losev[a] have found that basic dyes in aqueous solution are split by charcoal, the base being absorbed and the acid remaining as such in solution. The absorbents silk, wool, and cotton act similarly. The color base of crystal violet present in adsorbed condition upon the surface of the charcoal is a glittering brown-violet color; it is insoluble in water, but dissolves in acids, alcohols, pyridine, etc., with a blue-violet color. The color-base of "Neufuchsin" appears green on the surface of the charcoal and dissolves in acids, alcohols, pyridine, etc., with a red color. The body, described by Baeyer, obtained when fuchsine is treated with cold aqueous sodium hydroxide, and which is regarded as a polymeric imine base, resembles in many respects the material adsorbed on the charcoal. From crystal violet, also, there was obtained, by adding cold sodium hydroxide solution, a brown-violet amorphous powder difficultly soluble in water, but readily soluble in alcohols and pyridine with a blue-violet color. On these experimental grounds Freundlich and Losev suggest that amorphous polymerization products of the color base are adsorbed and form with carbon or other adsorbent, colloid complexes. In the case of the dyes patent-blue and orange IV, there is no splitting of the dye salt by charcoal on adsorption.

GELATINE.

SEPARATION OF ALUMINA FROM ITS SALTS.

Lummiere and Seyewetz[b] found that the separation of alumina from its salts could be effected by using gelatine as an absorbent.

SOIL.

ABSORPTION OF FERTILIZERS.

Selective absorption of different fertilizers by the soil was early studied by Frank[c] and by Treutler,[d] as described above.

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[a] Zeit. phys. Chem., **59**, 284 (1907).

[b] Bul. Soc. Chim., **35**, 676 (1906).

[c] Landw. Vers.-Stat., **8**, 45 (1866).

[d] Ibid., **12**, 184 (1869); **15**, 371 (1872).

PAPER.

ABSORPTION OF NEUTRAL SALTS AND DYES.

Schönbein[a] dipped strips of paper into different solutions, determined the heights to which the solution and the pure solvent rose in the paper, and observed their ratio. Since the paper absorbs the salt or organic coloring matter from solution, the higher layers are more and more dilute till near the top of the wetted paper one finds pure solvent. Göppelsröder[b] has used this selective property of paper to separate different dyes. He obtained a rose-red substance, probably fuchsine, from commercial azuline, which lost its violet tint and became a purer blue. Bayley[c] noticed that when drops of certain solutions fell on filter paper there was a separation into a water ring surrounding a solution more concentrated than the original solution. He found, too, that with increasing dilution the amount of separation became greater, and that increase in temperature and looseness of texture lowered the absorptive effect.

Lloyd[d] has determined the relative separations of different salts and finds that with sodium chloride no separation occurs, while sulphuric acid and solutions of ferric sulphate and of salts of silver, lead, and mercury suffer more or less separation into water and a stronger solution. Using the same method, Trey[e] has effected a separation of cadmium from copper. The copper cadmium solution is made alkaline with ammonia and diluted until the blue color is scarcely visible. Several drops of the solution are allowed to spread into a filter paper, and when the wet paper is subjected to ammonium sulphide vapor three rings appear—an outer water ring, which has been robbed of soluble material by the absorbing action of the paper; a yellow ring of cadmium sulphide precipitated from the soluble cadmium salt which was less strongly absorbed by the paper than the copper salt; and in the center is a black circle of mixed copper and cadmium sulphides, the copper salt being held back by the absorptive effect of the paper, while the liquid as a whole follows its normal tendency to spread, and thus the water appears to travel faster in the filter paper than the cadmium salt solution; the cadmium salt seems to spread slower than the water, but faster than the copper solution. Vriens[f] passed dilute nitric acid through several filter papers and found the absorption of acid, as shown by decrease in concentration, to be proportional to the number of filter papers used. J. J. Thomson[a] has made similar observations with filter paper. Fischer and Schmidner[b] allowed a saturated solution of ferrous ammonium sulphate to diffuse upwards through rolls of filter paper inside of a glass tube, and found that the proportion of the constituents in the filter paper was the same as in the double salt, although the absolute amounts had been diminished.

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[a] Verhandlung d. Naturforsch. Ges. in Basel, **3**, 249, (1861-63); Pogg. Ann., **114**, 275 (1861).

[b] Ibid., **3**, 263 (1861–63); Mitteil d. techn. Gewerbemuseums, Wien. (1889).

[c] Jour. Chem. Soc., **33**, 304 (1876).

[d] Chem. News, **51**, 51 (1885).

[e] Zeit. anal. Chem., **37**, 743 (1898).

[f] Zeit. phys. Chem., **31**, 230 (1899).

Cameron and Bell[c] have studied the rise of solutions and of pure solvents in paper, using aqueous solutions of malachite green, eosine, and potassium chloride, and mixtures of the two dye solutions and of eosine and potassium chloride. The rise of water and of solution is well represented by the equation $y^n = Kt$, where y is the height to which the paper is wetted, t is the time, and n and K are constants. They were able to separate the dyes from each other and from potassium chloride and showed that the presence of potassium chloride decreased markedly the height to which eosine rose in the paper in a given time.

COTTON.

ABSORPTION OF POTASH FROM POTASSIUM CHLORIDE SOLUTIONS.

These same investigators[d] wrapped strips of sensitive blue litmus paper in absorbent cotton moistened with distilled water freed from carbon dioxide and showing no reaction with a very sensitive specimen of litmus. A slight pressure was applied in order to insure intimate contact. In the course of about fifteen minutes the litmus paper had become decidedly pink, apparently showing an acid reaction. Two wads of this same cotton were placed in beakers, one containing a solution of potassium chloride neutral to litmus and the other containing potassium acetate with a slight but sufficient excess of acetic acid to redden litmus. Within a few minutes the supernatant liquor in the beaker containing potassium chloride had become distinctly acid, as shown by the further addition of litmus, while the supernatant solution in the beaker containing the acetate had become distinctly alkaline to both litmus and phenolphthalein. It is obvious, therefore, that the reddening of the litmus was a true absorption effect.

Absorbent cotton has the power of absorbing potash from a potassium chloride solution. A tube which was filled with absorbent cotton was placed in a beaker containing a solution of potassium chloride neutral to litmus. The solution after passing through the cotton was decidedly acid. But when potassium acetate was substituted for potassium chloride, even though a slight excess of acid was present, the solution after passing through the cotton was alkaline to litmus or phenolphthalein. Similar results were obtained by merely agitating wads of cotton in solutions of the reagents.

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[a] Applications of Dynamics to Physics and Chemistry (1888), p. 191.

[b] Ann. Chem. (Liebig), **272**, 156 (1893.)

[c] The Mineral Constituents of the Soil Solution, Bul. No. 30, Bureau of Soils, U. S. Dept. of Agr., (1905); Jour. Phys. Chem., **10**, 658 (1906).

[d] Bul. 30, Bureau of Soils, Dept. Agr. (1905).

BARIUM SULPHATE.

ABSORPTION OF SODA FROM SODIUM SULPHATE SOLUTION.

In another experiment a solution of sodium sulphate neutral to litmus was added to a solution of barium chloride neutral to litmus in the cold. After the precipitate subsided the supernatant solution was found to be acid. The experiment was repeated, using potassium sulphate instead of sodium sulphate, and the supernatant solution was alkaline. These experiments indicate that the barium sulphate precipitate absorbs some of the constituents of the solution, that the relative amount of acid and alkali absorbed may be varied, and that the absorbing medium may act very differently toward bases or acids.

KAOLIN.

E. C. Sullivan,[a] using magnesium and sodium chloride solutions, repeated Kohler's[b] experiments on the filtration of salt solutions through kaolin and confirmed his result that the filtrate from a neutral salt solution is slightly acid. Kohler attributed this effect to a selective concentration of dissolved substance—an adsorption of the base. But Sullivan accounts for this acidity in the filtrate by an exchange of the magnesium and sodium of these salts in part for the iron and aluminum of the kaolin, the salts of the latter metals undergoing extensive hydrolysis in dilute solution. The acidity observed is of the same order of magnitude as the quantity of trivalent bases found in dilute copper sulphate solution after contact with kaolin. He further suggests that the acidity of a salt solution after filtration through a substance, such as kaolin, through which the liquid diffuses but slowly, may be due to some extent to the greater velocity of diffusion of the acid constituent of the salt, which is present owing to hydrolysis, while the base is present (for salts of heavy metals) to a greater or less extent in the colloidal condition and colloids are marked by their very slow rate of diffusion.

COPPER HYDROXIDE.

Tommasi[c] found that the solutions of such neutral salts as sodium chloride and sulphate and potassium chloride and bromide become basic when precipitated copper hydroxide is added to the solution. The acid is absorbed by the copper hydroxide, which then becomes green in color.

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[a] The Interaction Between Minerals and Water Solutions, Bul. 312, U. S. Geol. Survey, p. 8, 1907.

[b] Zeit. prakt. Geol., **11**, 49 (1903).

[c] Compt. rend., **92**, 453 (1881).

NEGATIVE ABSORPTION.

CHARCOAL.

Lagergren[a] found that either solvent or solute could be absorbed, or, in other words, that the solution could become more concentrated or less concentrated. Thus solutions of sodium chloride, potassium chloride, ammonium chloride, and ammonium bromide became more concentrated after contact with charcoal, while sodium nitrate, potassium nitrate, sodium sulphate, potassium sulphate, and ammonium nitrate become less concentrated. This author states that he could find no evidence of any change in alkalinity or acidity of the solutions. This behavior has been ascribed by the author to an increase in the density at the surface of the solid—an increase in density which involves an increase in pressure. If, therefore, an increase of pressure increases the solubility, or, in other words, if solubility is accompanied by a decrease of volume, there will be a positive absorption; but under reverse conditions there will be a negative absorption. Lagergren has calculated the degree of absorption from the surface of the solid exposed, the radius of molecular action, and the density of water under different pressures. The results of the calculation for absorption of ammonium chloride and the observed absorption agree fairly well.

KAOLIN AND GLASS WOOL.

Parallel results have been obtained where the absorbing material is kaolin and glass wool, the negative absorption of sodium chloride by kaolin having been found by van Bemmelen.[b]

CLAY.

White china clay has been used as an absorbing medium by Cushman,[c] who finds a considerable decrease in the basic ions from solutions of ammonium chloride, barium chloride, and aluminum sulphate. The data indicate that there may have been also a negative absorption of the sulphuric acid, i. e., a considerable absorption of water from aluminum sulphate solutions, which then became more concentrated with sulphuric acid, although the author thinks the phenomenon is due entirely to the fact that, owing to hydrolysis, free acid necessarily exists in a solution of a salt of a trivalent base.

SELECTIVE ABSORPTION OF DYES.

Dyes forming colloidal solutions are extremely sensitive to electrolytes in regard to their adsorption[d], the effect being proportional to the size of the colloidal particles. In the case of electro-negative dyes (Congo-red) cations facilitate absorption, anions depress it; with electro-positive dyes (toluidine-blue) the opposite is seen, but in both cases the effect of anions is small. Salts of the heavy metals which form positively charged colloidal hydroxides powerfully promote adsorption of Congo-red. The facilitating ion is carried down with the dye. The presence of a stable colloid, such as gelatine, protects Congo-red from the action of electrolytes. When gelatine is precipitated by tannin, its adsorbed electrolytes are split off. In the process of blood-clotting there is a diminution of electrical conductivity, ions (probably of calcium) disappearing from solution. There is no evidence of a sudden separation of electrolytes in the tissues at the moment of death, although there is a gradual one when a living tissue is warmed from 11° to 56°. In the action of rennet on milk there is a slight increase in conductivity, an additional fact showing this process to be quite different from blood-clotting. In all probability rennet action is only an expression of pepsin action in neutral or faintly alkaline media (Pawloff).

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[a] Bihang till K. Sv. Vet. Akad. Handl., **24**, Afd. II. No. 4 (1898).

[b] Zeit. anorg. Chem., **23**, 321 (1900).

[c] Bul. No. 92, Bureau of Chemistry, U. S. Dept. Agr., 1905, p. 18.

[d] Bayliss, Biochem. Jour., **1**, 175 (1906).

Recently Craw[a] has studied the filtration of crystalloids and colloids through Martin's gelatine filter (a Pasteur-Chamberland filter the pores of which are filled with solid gelatine) and finds it highly but not completely permeable for such crystalloids as sodium chloride, potassium iodide, and butyric acid. The work of Waymouth Reid showing that this filter is slightly permeable to colloids was confirmed. As filtration proceeds the crystalloids show an increasing concentration in the filtrate, whereas the colloids gradually decrease to zero and are completely retained by the filter. The presence of one substance in solution often affects the rate of filtration of another. The permeability depends, too, upon the gelatine used. Thus a filter prepared with 15 per cent gelatine solution is less permeable to certain colloids than a filter prepared with 7.5 per cent gelatine solution, and formalized gelatine is less permeable to sodium chloride than ordinary gelatine.

APPLICATION OF SELECTIVE ABSORPTION IN PHYSIOLOGY.

The theories of absorption have been applied to physiology in a research on the neutralization by lysin and by antilysin and on diffusion through gelatine filters.[b]

SELECTIVE ABSORPTION OF DYES BY SOILS.

Sjollema[c] found that different solid soil constituents have very different absorptive power for dyes. He classifies as colloids those substances which are colored by organic dyes, and thus excludes undecomposed mineral fragments and quartz which are not tinted by the dyes he used. The definition of a colloid thus implied is so inclusive as to bring such substances as carbon black, platinum black, and all other amorphous substances, as well as powdered crystalline substances, under the head of colloids, and consequently it becomes meaningless. It has been shown[a] by Cameron and Patten that gentian violet (*gentianin*) is adsorbed by quartz to a considerable extent, and this same dye colors other soil grains, crystalline as well as amorphous.

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[a] Proc. Roy. Soc., B **77**, 311 (1906).

[b] Craw. Zeit. phys. Chem., **52**, 585 (1905).

[c] Jour. f. Landw., **53**, 67 (1905).

Cameron and Bell[b] found that solutions of dyes poured through soils always yield clear water for the first runnings. When eosin solution is used the dye soon appears in the percolate, but soils retain methylene blue, malachite green, gentian violet, and some other dyes with remarkable tenacity. Separations of a mixture of eosin and methylene blue were made by percolation, the methylene blue being completely retained by the soil, while the eosin was comparatively readily removed by washing. It was shown, too, that for any particular solution of a dye the various soils had a definite absorption limit; that is, if the solution is poured on a given mass of soil slowly and at a very uniform rate there is a point at which the soil will cease to absorb the dye, and the solution will come through unchanged. Fairly good duplicate determinations for the absorptive power of any particular soil can be made in this way. Heavy soils absorb generally more than light soils, and black, red, or dark-brown soils more than those of lighter color. The presence of humus adds very considerably to the absorptive power of a soil. In some cases, at least, the absorption of one dye by a soil does not materially reduce its capacity for retaining a second dye. It was found, too, that while a dye might be so firmly held by a soil as to resist removal on leaching, the soil nevertheless gave up dye to filter paper and to some kinds of blotting paper. Likewise, absorbed dye may be removed unchanged in some instances by use of a different solvent—for example, alcohol—when further leaching with water is practically of no avail. These authors state that, in general, papers are better absorbents for dyes than soils, but, on the other hand, some solutes, such as alkalies, are generally absorbed more powerfully by soils than by papers. This has an important bearing on the common practice of testing the reaction of a soil with moist litmus paper. Blue litmus, as is well known, is the sodium salt of the red dye. In aqueous solution it must be considerably hydrolized, so that when a paper saturated with it is brought into intimate contact with a soil the base is absorbed more readily by the soil and the remaining acid more readily by the paper, with the consequence that the latter becomes red. This explanation of the reddening of litmus paper by soils was confirmed by other experiments.

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[a] Jour. Phys. Chem., **11**, 581 (1907); Trans. Am. Electrochem. Soc., **10**, 67 (1906).

[b] The Mineral Constituents of the Soil, Bul. 30, Bureau of Soils, U. S. Dept. of Agr., 1905, p. 57.

SELECTIVE ABSORPTION AND THE ACIDITY TEST FOR SOILS.

Cameron and Bell further suggest that it might be argued from these experiments that the only test as to the presence of an acid in a soil is the formation of an acid solution when extracted with water. It is true that this is the only satisfactory criterion which suggests itself. As the experiments just cited show, solid and other absorbent substances can and do absorb acids, some more than others, and it is quite possible that an absorbed acid, which was not easily removed from a soil by water, might be removed by paper, if paper were the better absorber for that particular acid. It is well, therefore, to view with caution the prevalent notions as to the wide distribution of acid soils founded on a very uncertain criterion, and especially in view of the fact that the great majority of soils yield aqueous extracts which on heating in platinum show alkaline reactions. Most of our field crops can withstand a fairly high concentration of acid; but clover[a] is especially sensitive, being inhibited in growth by concentrations less than twenty-thousandth normal (N/20,000). Yet cases have been observed where clover was found growing well in soils apparently very acid, the true explanation being undoubtedly that the supposed estimation of acidity was, in fact, a measurement of the absorptive capacity of the soil.

Furthermore, it is probably fallacious to assume that the acidity of a soil can be estimated by adding calcium hydrate, ammonia, or other alkalies in solution until the soil will turn red litmus paper blue when the paper is brought into contact with the soil, since it has been clearly shown that most soils absorb these substances much more effectively than does litmus paper. If these solutions be added to the soil slowly (for absorption is not an instantaneous process, but requires appreciable time to attain equilibrium), it frequently is astonishing how much alkali can be taken up before an alkaline reaction can be detected by the test paper—a fact repeatedly observed by various investigators, but the significance of which had not hitherto been recognized.

GENERAL STATEMENT CONCERNING SELECTIVE ABSORPTION BY SOILS.

Regarding the degree to which the different constituents of the soil solution are absorbed, several generalizations can be made; but from the foregoing data and discussion it will be evident that each soil will exert its own peculiar effect in retaining soluble matter, and that, while we may seek to classify a fertilizer as adding potassium or nitrates or phosphates to the soil, the *form* or *salt* in which the fertilizer is added will affect its absorption by soil.

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[a] Cameron and Breazeale, Jour. Phys. Chem., 8, 1 (1904).

Of the basic radicals, potassium is most strongly bound by the soil. If a soil is saturated with potassium, then one may replace the more recently absorbed potassium by other bases merely by treating the soil repeatedly with a solution of another solute, for the potassium is distributed each time between the soil and solution, and of course when the solution is removed from contact with the soil the potassium is withdrawn, too, and can exercise no further effect upon the equilibrium. Meanwhile the soil is absorbing the base or bases in these solutions applied to the soil to remove potassium. In effect we have replaced potassium by another base or bases; but it by no means follows that we may have here a case of chemical exchange by a rearrangement of definite compounds, especially as the replacement need not follow the chemical equivalence of the bases involved. This predominant retention of potassium by soils is undoubtedly the main reason why potassium is so little in evidence among the soluble salts of alkali soils—salts which have come up through the lower layers of soil and finally been concentrated near the surface, sodium and calcium salts passing on up to the surface, and, to a less extent, the magnesium salts also. It is true that in general the magnesium silicates are quite readily soluble and much hydrolyzed by water, but magnesium is absorbed to a much greater extent than calcium or sodium, although to a lesser extent than potassium.

ABSORPTION FROM VARIOUS SOLVENTS.

PICRIC ACID IN WATER, ALCOHOL, AND BENZENE.

The experiments by Walker and Appleyard[a] on absorption by silk have shown that while picric acid is absorbed by silk from solutions in water and alcohol, yet in benzene solution there was no absorption. The nature of the solvent plays, therefore, an important rôle. The relative solubilities of picric acid in the three solvents do not throw any light on the absorptive power from the different solvents, for the solubility of picric acid in benzene lies between the solubility in water and that in alcohol.

DYES IN PETROLEUM, BENZENE, XYLENE, CARBON TETRACHLORIDE, AND CARBON DISULPHIDE.

Tsvett[b] has shown that many dyes dissolved in light petroleum, benzene, xylene, carbon tetrachloride, or carbon disulphide are precipitated by powdered substances, from which they may be extracted by alcohol, ether, acetone, or chloroform. There is further an adsorption series in which the substances can replace each other on the absorbent. When a mixed solution, as, for instance, chlorophyll dissolved in carbon disulphide, is filtered through a column of precipitated calcium carbonate, the dyes are precipitated, but mutually replace each other and arrange themselves according to the adsorption series in the direction of the stream. If any zone is not pure, it can be extracted and the adsorption repeated until the desired degree of purity is attained.

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[a] Jour. Chem. Soc., **69**, 1334 (1896).

[b] Chem. Centr., 1906, ii, 1286; from Ber. deutsch. bot. Ges., **24**, 384–393.

MAGNITUDE OF ABSORPTION IN DIFFERENT SOLVENTS.

Rosenthaler and Türk,[a] in studying the effect of the solvent upon the degree of absorption, found that it is greatest from aqueous solutions. The absorption is less from solutions in ethyl alcohol, methyl alcohol, ethyl acetate, acetone, and chloroform, in the order named.

Freundlich, in his recent paper on absorption, has compared the absorption for a number of different solvents, and for dilute solution it appears to have the same order of magnitude in all of the different solvents; but, while in the same order of magnitude, there are really differences, which become more pronounced as the concentration increases, and are widely different in strong solutions.

DISTRIBUTION.

The earlier investigators appear to have had no true conception of the distribution of a substance between the liquid and solid material. Salomon[b] agrees with Liebig that absorption is purely physical in nature, but does not consider the concentration of the end solution left above the solid.

Biedermann[c] also plots as abscissa the quantity of soil per hundred parts of solution and as ordinate the percentage of solute absorbed from solution. This is a very useful and practical method of representing results, but fails to give a clear idea of the phenomena of distribution, which is tacitly assumed in Biedermann's work.

POTASSIUM BETWEEN SOIL AND SOLUTION.

Peters's[d] results on the absorption of potassium chloride by a soil have been recalculated in Table III to show the quantities of potassium in unit quantities of a solution and a soil. He neglected, however, the chlorine; but it is altogether likely that less of it would have been found absorbed than corresponds with the absorbed potassium. It is safe, therefore, to assume that Peters's analytical data give a representative distribution curve for the basic radical potassium between a soil and water. To bring out more clearly the enormous effect exercised by the soil in withdrawing soluble material from solution, the percentage of potassium absorbed by the soil from solution is given for each concentration in the accompanying table. It will be seen that this absorptive effect is nearly twice as great with dilute solution as in the strongest solution used, varying from 94 per cent of the total potassium present in the dilute solution to 54.9 per cent for a solution 20 times stronger.

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[a] Arch. Pharm., **244**, 517 (1906).

[b] Landw. Vers.-Stat., **9**, 351 (1867).

[c] Landw. Vers.-Stat., **11**, 1 (1869).

[d] Landw. Vers.-Stat., **2**, 129 (1860).

TABLE III.—*Distribution of potassium between soil and solution of potassium chloride, according to Peters.*

Potassium per kilo soil.	Potassium per liter of solution.	Total potassium present absorbed by soil.	Potassium per kilo soil.	Potassium per liter of solution.	Total potassium present absorbed by soil.
Grams.	*Gram.*	*Per cent.*	*Grams.*	*Grams.*	*Per cent.*
1.011	0.0648	94.0	1.390	0.127	91.6
1.096	.0628	94.5	1.453	.203	87.9
1.168	.0677	89.2	1.511	.361	80.7
1.238	.0797	94.0	1.579	.679	70.3
1.328	.089	93.8	1.610	1.310	54.9

CALCIUM BETWEEN SOIL AND SOLUTION.

Peters has also determined the quantity of calcium extracted from the soil by the same solutions which were being studied with respect to the absorption of potassium. He found that calcium is distributed in a manner nearly analogous to potassium, and that the curve for the distribution of calcium between soil and water has apparently the same general form as that for potassium. This observation indicates that the absorption of two solutes may proceed almost independently of each other, at least when the concentrations of both are low.

HYDROCHLORIC ACID BETWEEN CARBON BLACK AND SOLUTION.

When carbon black is shaken with an aqueous solution of hydrochloric acid, Kelberin[a] found that there is a perfectly definite distribution ratio; the results could be duplicated to within a fraction of 1 per cent.

INCONSTANCY OF DISTRIBUTION RATIO.

Kroeker[b] studied the relation between absorption and time of contact, quantity of carbon, and concentration of solution, and found that the distribution ratio between carbon and solution is not constant, but that relatively more is absorbed from dilute solutions than from strong. Schmidt[c], using Van Bemmelen's data[d] has sought to show that the distribution ratio of potassium sulphate, potassium nitrate, potassium chloride, sulphuric acid, hydrochloric acid, and nitric acid was constant. This result has been contested by Van Bemmelen,[a] who points out that the distribution ratio of a substance between solid and liquid need not necessarily be constant in the case of equilibrium between solid and liquid solutions.

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[a] See Ostwald, Lehrbuch der allgemeine Chemie (1891), p. 1096.

[b] Über die Adsorption gelöster Körper durch Kohle, Dis., Berlin (1892).

[c] Zeit. phys. Chem., **15**, 56 (1894).

[d] Jour. prakt. Chem., **131**, 324 (1881).

DISTRIBUTION FORMULAS.

A number of investigators[b] have advanced formulas to express the distribution of a solute between a solvent and an absorbing medium. These expressions have been generally suggested by the apparent analogy to the distribution of the solute between two immiscible solvents, for which two general equations have been proposed.

If c be the concentration of the solute in one solvent and c_1 the concentration of the other, then when there is no association of solute in either solvent the distribution is described by the formula $c/c_1 = K$; but if there be association of solute in either solvent, the formula becomes $\frac{c^n}{c_1} = K$. K is a constant for any standard conditions of temperature.

Ostwald[c] has proposed this same form of equation slightly modified, $x/m = \alpha\, C^{\frac{1}{p}}$, where x is the total mass of solute absorbed and m is the mass of the absorbent; C is the concentration of the solution, and p and α are constants.

This exponential formula has been found to hold more or less well for a number of cases of absorption, of which a few will be cited. Thus Schmidt[d] found it held for the absorption of iodine and several acids by charcoal, but it did not hold for the absorption of picric acid by cellulose or of eosine or malachite green by silk. Küster[e] found such a relation held for the absorption of iodine by starch.

Walker and Appleyard[f] have studied a case of unusual interest. They found that the distribution of picric acid between water and silk was described by the formula $\frac{S}{W^{\frac{1}{2.7}}} = 35.5$, where S represented concentration of the dye in the silk and W the concentration in water. This would indicate that at the concentration studied the molecule of picric acid in the water solution is 2.7 times as large as that represented by the formula $C_6H_2(NO_2)_3OH$, at least; but this is negatived by the cryoscopic measurements of the osmotic pressure and of the conductivities of aqueous solutions of picric acid.

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[a] Zeit. phys. Chem., **18**, 331 (1895).

[b] Schmidt, Zeit. phys. Chem., **15**, 60 (1894); Küster, Annalen, **283**, 360 (1894); Walker and Appleyard, Jour. Chem. Soc., **69**, 1334 (1896); Biltz, Ber. deutsch. chem. Ges., **37**, 1766 (1900); **38**, 2963, 2973, 4143 (1905); Zacharias, Zeit. phys. Chem., **39**, 468 (1901).

[c] Lehrbuch der Allgemeine Chemie II. (2 Aufl.), 232.

[d] Zeit. phys. Chem., **15**, 60 (1894).

[e] Annalen, **283**, 360 (1894).

[f] Jour. Chem. Soc., **69**, 1334 (1896).

Biltz[a] has studied several similar cases. An especially interesting one is the absorption of alizarin by ferric oxide, the distribution being described by an exponential formula, but the curve representing it not going through the origin. That is, the concentration of the solution must be above a certain value before any absorption on the solid can take place. Similar cases, as, for instance, in the absorption of phosphates from solution by soils, have been observed in this laboratory.

Freundlich[b] has added to Ostwald's equation the concept that the total quantity of solute present in the system has an effect upon the equilibrium—though the explanation for this is not yet at hand—and his empirical equation, derived from Ostwald's, takes the form $\lambda = \frac{V}{m} ln\left(\frac{a}{a-x}\right)$, where λ is a constant, V is the volume of solution, m the mass of absorbent, a the total solute in the system, and x the total quantity of solute obsorbed. Freundlich restricts this formula to dilute solutions and finds that it does not hold for solutions which conduct electricity well.

Travers[c] objects to Freundlich's statement that adsorption is independent of the solid adsorbent, the solute, or the solvent used, and, in addition, makes the point that a rigid distinction between crystalline solid solutions and highly viscous liquid solutions, such as glass, should be made. According to Travers, many cases of absorption which Freundlich would class as purely adsorption effects are in reality highly viscous liquid solutions formed at the surface of the adsorbing solid.

Freundlich[d] in his answer to Travers states that he has not thought that the *magnitude* of the adsorption effect is independent of the solid adsorbent, the solute, and the solvent, but merely that the same solid adsorbs different solutes from solution in the same relative quantities from different solvents.

Travers also takes exception to Freundlich's statement that the magnitude of adsorption is independent of the temperature. Freundlich admits that, broadly speaking, Travers's criticism is justified. Freundlich means merely to indicate that the temperature effect is so slight as to render unnecessary the use of a thermostat in the measurements made by himself.

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[a] Ber. deutsch. chem. Ges., **37**, 1766, 3138 (1904); **38**, 2963, 2973, 4143 (1905). Nach. K. Ges. Wiss. Göttingen, Math.-Phys. Klasse, **1**, 1 (1904); **1**, 1 (1905); **3**, 1 (1905), with Kurt Utescher.

[b] Zeit. phys. Chem., **57**, 385 (1906).

[c] Zeit. Phys. Chem., **61**, 241 (1907).

[d] Zeit. Phys. Chem., **61**, 249 (1907).

Hedin[a] has shown that charcoal absorbs trypsin almost completely from dilute solution, and as the concentration of trypsin increases the charcoal gradually becomes saturated. Arguing from Freundlich's[b] treatment of adsorption, Hedin concludes that this behavior of trypsin is different from that of adsorbed crystalloids, in that the trypsin shows a specific attraction for the charcoal, the first portions adsorbed being so strongly bound as to suggest an irreversible process. But in reality Hedin's observation with trypsin agrees with numerous systems where the adsorbed solute is a crystalloid.[c]

SULPHURIC AND HYDROCHLORIC ACIDS BETWEEN TEXTILES AND SOLUTIONS.

Vignon and Mollard[d] have shown the distribution of sulphuric and of hydrochloric acids between their respective aqueous solutions and the textiles unbleached silk, ungummed silk (soire décreusée), cotton, and linen. They find that cotton does not absorb these acids, but silk and linen take up relatively more acid from dilute than from concentrated solution, the coefficient of distribution $\frac{C_2}{C_1}$ increasing greatly as the acids are diluted, and decreasing slightly with rise in temperature. Equilibrium is established within one hour in those systems where the strength of acid was in round numbers from 1 per cent to 0.1 per cent. From 100 c. c. to 400 c. c. of solution was maintained in contact with 10 grams of the textile absorbent. This research establishes the fact of distribution in these systems, but the data is insufficient to give the function $\phi\ (C_2) = C_1$, even approximately.[e]

SALTS BETWEEN GELATINE AND SOLUTION.

Bayliss[f] has found that the curve of electrical conductivity of successive distilled water extracts of gelatine is a hyperbola. It is therefore impossible to wash out all the electrolytes except by an infinite number of changes of distilled water, each change removing a less percentage than the previous one; in other words, the electrolytes are present in an absorbed form. When the gelatine is washed nearly free from such admixtures and is placed in solutions of electrolytes, it again absorbs them, and so the conductivity of the solution is diminished. But it must not be taken as established that an absorbed solute is unable to contribute to the electrical conductivity of the system in which it exists. It has been shown by Patten[a] that soil grains which have absorbed alkali carbonates, when in aqueous suspension, add very greatly to the electrical conductivity, and when removed by centrifuging take with them the adsorbed or absorbed material, leaving the supernatant solution lower in conductivity than before. Similarly soils made up to paste with water or salt solution show an electrical conductivity due in part to salt which is adsorbed (or absorbed) and is very resistant to removal by leaching.[b]

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[a] Hoppe-Seyler's Zeit. physiol. Chem., 5, 504 (1907); see also Hedin, Bio.-Chem. Jour., **2**. Biltz, Zeit. phys. Chem., **47**, 615 (1904); Nernst, Zeit. Elektrochem., **10**, 377 (1904); Craw, Zeit. phys. Chem., **52**, 569 (1905).

[b] Zeit. phys. Chem., **57**, 385 (1906).

[c] Freundlich's restriction of the validity of his formula to *dilute solution* and to *solutes which do not yield conducting solutions* tacitly admits the very point Hedin is making, i. e., that adsorption is a specific effect which depends *primarily* upon the composition of the adsorbent, of the solute, and of the solvent. The lowering or raising of the surface tension, *solid-liquid,* upon which Freundlich bases his treatment, is controlled by the composition of the solid and of the liquid which constitute the liquid-solid surface.

[d] Bul. Soc. Chim. (3), **36**, 1304 (1906); Compt. rend., **143**, 550 (1906); see also Knecht, Rawson, Löwenthal, Handbuch der Färbung von Spinnfassern.

[e] See also Vignon, Bul. Soc. Chim. (4), **1**, **2**, 273 (1907) on the relation of the electrical conductivity of the dye solution to its efficiency in coloring.

[f] Bio.-Chem. Jour., **1**, 175 (1906).

FERRIC CHLORIDE BETWEEN FERRIC HYDROXIDE AND SOLUTION.

Duclaux[c] opposes the contention of Nicolardot and Wyrouboff that the formation of a compound $Fe_2(OH)_6 \frac{1}{150} Fe_2Cl_6$ limits the possibility of removing chloride from colloidal ferric hydroxide. Duclaux has obtained by dialysis a ferric hydroxide containing less than one-third of the amount of chloride implied by the above formula, and sees no reason why the removal of chloride should not be carried further.

DEFINITIONS.

MAXIMUM ABSORPTIVE CAPACITY.

The maximum amount of a solute which an absorbent may remove from solution is, under any standard conditions of temperature, a perfectly definite quantity, characteristic of the absorbent, and is a measure of what may be defined as the "maximum absorptive capacity" of an absorbent. This maximum amount of solute can not, however, be absorbed from a solution of any concentration whatever, as is shown by equilibrium experiments,[d] but only from a solution which is saturated with respect to the solute and at the same time in equilibrium with the absorbent. Practically this case could only be realized when some of the solute is present as a solid phase, and such a system has generally but little interest, owing to the difficulty of distinguishing between the absorbed and nonabsorbed solid. It is, therefore, more convenient to estimate the maximum absorptive capacity of an absorbent by extrapolating from data obtained with solutions somewhat below saturation.

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[a] Electrochem. and Met. Ind. 5, 257 (1907).

[b] Whitney and Means, Division of Soils, U. S. Dept. Agr., Bul. 8, 1897.

[c] Compt. rend. **143**, 296 (1906).

[d] Cameron and Bell, Bul. No. 30, Bureau of Soils, U. S. Dept. Agr. 1905; Schreiner and Failyer, Bul. No. 32, Bureau of Soils, U. S. Dept. Agr. 1906; Patten, Trans. Am. Electrochem. Soc., **10**, 67 (1906).

SPECIFIC ABSORPTIVE CAPACITY.

From a solution containing less solute than is required to saturate it an absorbent can remove a quantity less than that which measures its maximum absorptive capacity, but a quantity which is nevertheless perfectly definite for any given concentration of solution. This quantity may be defined as the specific absorption with respect to that particular solution.

Thus a solution of potassium chloride containing 500 parts per million of potassium chloride when brought into contact with a soil will lose potassium chloride, as the soil absorbs it, at a speed which gradually decreases till the salt reaches a final distribution between soil and solution. The weight of potassium chloride absorbed at a given temperature by 1 gram of soil represents the specific absorptive capacity of the soil for that particular salt at that particular concentration of the salt. This concentration is not the original concentration of solution—500 parts per million of potassium chloride—but is the final concentration reached after the absorption has been completed. If by a slight alteration of other conditions, such as temperature, the soil absorbs temporarily more salt than when the chosen temperature is again reached, the solution will remove the excess of absorbed salt from the soil and reduce the quantity of potassium chloride remaining in the soil to its absorptive capacity for the original conditions. In other words, absorption is a reversible phenomenon.

GENTIAN VIOLET DYE BETWEEN SOIL AND SOLUTION.

It is significant that those substances which are prominent as fertilizer constituents, namely, potassium, calcium, ammonia, phosphoric acid, and proteid organic matter, are substances which are markedly absorbed by soils. From the increasing knowledge of the effect of adsorbing surfaces upon the chemical reactions which might ordinarily be expected to take place among these various soil constituents, it is evident that such reactions may be and probably are very much modified when they take place in the presence of the adsorbing surfaces. In studying the distribution of an added solute between a soil and water there is difficulty in obtaining complete data when the soil already contains the solute in question. There is no method of determining absolutely the quantity of any soluble material in a soil which has already been absorbed on the soil grains, and even though the amount of solute present in the water added to the soil be measured exactly, the total amount present as absorbed material can not be ascertained.

To determine the character of this distribution more readily, water-soluble bodies have been used which are not contained in the soil naturally, and which are not appreciably changed by contact with the soil. Thus there are known the quantities of solute, of the soil, and of the water, and by varying the weight of solute a series of systems in equilibrium are obtained and the distribution of solute between water and soil can be examined quantitatively. When the character of the distribution is thus determined, a criterion is obtained for comparison with the less exact data of the distribution observed with soluble bodies which commonly exist in the soil, such as potassium salts, nitrates, phosphates, or water-soluble organic matter. Similar equilibrium experiments were made using fine quartz flour instead of soil to eliminate the effect of (1) the soluble material already present in the soil and (2) of the organic matter in the soil, which latter exerts so large an absorbing effect upon the solute as to mask the distribution of this solute between the mineral components of the soil and the solution.

The dye gentian violet has been found particularly well adapted to studying distribution, because it is changed very slightly, if at all, by contact with the soils used or with quartz flour, and because it can be readily estimated colorimetrically to within a fraction of a part in a million of solution. It is a basic dye (gentianin), represented by the formula $(CH_3)_2N.C_6H_3:SCl.N:C_6H_3.NH_2$, and is analogous in that respect to ammonia bases in general and to some fermented manures. The sample of gentian violet used gave characteristic reactions, viz: (1) Dilute aqueous acids, as hydrochloric or nitric acids, turn the aqueous dye from a violet to green; (2) concentrated sulphuric acid dissolves the dye, forming a yellowish-green solution, and (3) aqueous sodium hydroxide gives a violet color. The solubility of gentian violet in water at 25° C. was found to be 6.81 per cent of solution by weight. The experiments were carried out at room temperature which varied but little from 25° C.

One hundred gram portions of each soil were placed in strong glass bottles of some 225 c. c. capacity, with 150 c. c. of dye solution, agitated in a shaker for several days, placed in a centrifuge and whirled for several hours, and a small portion of the liquid withdrawn from each and the dye content estimated colorimetrically. The bottles were then replaced in the shaker, again centrifuged, and the dye in solution again determined. This was repeated till equilibrium had been reached, which usually required about a week's time.

By a separate experiment it was found that 100 grams Marshall silt loam absorb 4 c.c. of water from a saturated atmosphere at 29° C. This was taken as representing the volume of water which is extracted from the solution when brought into contact with this soil. So, in effect, the volume of solution for which the concentration of dye is determined is not 150 c.c.—the volume of liquid added—but 146 c.c. Similarly, 100 grams Hagerstown loam absorbs 4.5 c.c. of water from a saturated atmosphere at 29° C., and accordingly this value was used in calculating the concentration of the solutions after absorption. The quartz flour used absorbed 0.8 c.c. water under the same conditions; but as this correction affects the distribution curve by less than 1 per cent, it is neglected.

Table IV gives the experimental data for the distribution of gentian violet between soil and water. The first column shows the total quantity of dye added; the weight of dye withdrawn from solution per kilo of soil is shown in the second column for Marshall silt loam, a representative fertile soil, and the grams of dye remaining in a liter of solution in the third column. The distribution for Hagerstown loam, another fertile soil, is given similarly in the fourth and fifth columns, and for fine quartz flour in the sixth and seventh columns.

Table IV.—*The distribution of gentian violet between soils and solution.*

[100 grams soil and 150 c.c. solution.]

Dye added.	Distribution.					
	Marshall silt loam.		Hagerstown loam.		Quartz flour.	
	Dye per kilo soil.	Dye per liter solution.	Dye per kilo soil.	Dye per liter solution.	Dye per kilo soil.	Dye per liter solution.
Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
0.005					0.06	Trace.
.015					.14	0.0001
.075					.743	.0040
.100					.984	.0108
.200			1.9996	0.00023	1.901	.066
.300	3.00	Trace.			2.66	.224
.40			3.9998	.00140	2.89	.740
.50	4.85	0.0001	4.9996	.00250	2.95	1.370
.70					2.97	2.668
1.00	9.999	.00083	9.9825	.0120	2.93	4.710
1.50			14.95	.0325		
2.00	19.99	.006	19.817	.1250		
2.50	24.97	.020			2.90	14.75
3.00	29.91	.060	20.45	6.525		
3.20	31.89	.070				
4.00	37.00	2.050	20.25	13.500		

When the concentration of the dye left in solution is taken as abscissa and the concentration in soil as ordinate, curves resembling the parabola are obtained. By extrapolating these curves the maximum absorptive capacity of the soil for gentian violet may be found: Marshall silt loam, 38 grams dye per kilo of soil; Hagerstown loam, 20.45 grams dye per kilo; quartz flour, 2.97 grams dye per kilo. The absorption capacities are in the ratio 113: 61 : 1, and show that each soil has its own absorptive capacity. The soil grain area of Marshall silt loam is very nearly the same as that of Hagerstown loam when calculated on the basis of their mechanical analysis, and yet the Marshall soil absorbs nearly twice the quantity of dye taken up by the Hagerstown soil. Again, both of these soils have an area presented by their grains nearly twice as great as the surface offered by the same weight of the quartz flour used, and yet the quartz has by no means half the absorptive capacity of either of the soils. The presence of organic matter is undoubtedly a very important factor in determining the magnitude of the absorption; but this absorption of dye by quartz shows that the mineral constituents of a soil, as well as the organic matter it contains, enter in to determine its absorptive capacity. It is certain, moreover, that mineral constituents other than gelatinized products of hydrolysis are capable of absorbing soluble bodies from the soil solution to a marked extent.

Considering the concentrations of dye when the soil has nearly reached its maximum absorptive capacity, it will be seen in Table IV that Marshall silt loam abstracted from solution 92.5 per cent of the total dye added; the Hagerstown loam, 51.1 per cent; and the quartz flour, 59 per cent. At lower concentrations of dye in solution the soils absorbed relatively more dye, and although the dye is truly distributed between soil and solution the soil holds so large a portion of dye that for practical purposes the dye is all absorbed. Thus for 0.5 gram dye added the Marshall silt loam absorbed 97 per cent; the Hagerstown loam, 99.99 per cent; and the quartz flour, 59 per cent of the dye. When only 0.075 gram dye is added, the quartz flour absorbs 99 per cent, leaving only 1 per cent in solution. Consequently it is clear that absorption experiments carried on over a limited range of concentrations may lead to false conclusions regarding the distribution. These experiments further emphasize the fact that a soil may hold a relatively large quantity of water-soluble material even in contact with a very dilute aqueous solution.

EOSINE DYE BETWEEN QUARTZ FLOUR AND SOLUTION.

Table V gives the data for the distribution of sodium eosine between quartz flour and water. Here the absorptive capacity of the quartz for eosine does not tend to a limiting value—at these concentrations—as it does for gentian violet, but the absorption of eosine is nearly proportional to the quantity of eosine in solution, the distribution curve being not quite a straight line. Examples of linear distribution are known. For instance, Gaubert[a] observed it for the absorption of methylene blue by crystals of phthalic acid deposited from solution in the dye when the solution is cooled, and for the absorption of the same dye by crystals of nitrate of urea. And Van Bemmelen[b] has given an interesting case in the absorption of potassium chloride by stannic oxide.

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[a] Compt. rend., **142**, 936 (1906).

[b] Zeit. anorg. Chem., **23**, 113 (1900).

TABLE V.—*Distribution of eosine between quartz flour and solution.*

[50 grams quartz and 75 c. c. solution.]

Dye added.	Distribution.		Dye added.	Distribution.	
	Dye absorbed per kilo quartz.	Dye per liter of solution.		Dye absorbed per kilo quartz.	Dye per liter of solution.
Gram.	*Gram.*	*Gram.*	*Gram.*	*Grams.*	*Grams.*
0.00242	0.009	0.027	0.075	0.348	0.768
.0075	.0135	.091	.75	4.2	7.200
.0248	.085	.274			

MANURE EXTRACT BETWEEN SOIL AND SOLUTION.

To study the absorption of the soluble organic bodies in manures, several concentrations of a well fermented and matured extract were allowed to stand in contact with soils, with frequent shaking, for two weeks at room temperature, 25° C. Then the supernatant liquid was poured off, centrifuged, evaporated to dryness in a steam bath, then in a water oven, and weighed; ignited, weighed, and the organic matter gotten by difference. The quantity of organic matter in the original manure-extract solution was determined similarly.

TABLE VI.—*Distribution of manure extract between soil and solution.*

[500 grams soil and 2,000 c. c. solution.]

Organic matter in added extract.	Hagerstown loam.		Marshall silt loam.		Norfolk sand.	
	Organic matter absorbed per kilo soil.	Organic matter per liter solution.	Organic matter absorbed per kilo soil.	Organic matter per liter solution.	Organic matter absorbed per kilo soil.	Organic matter per liter solution.
Grams.	*Grams.*	*Gram.*	*Gram.*	*Gram.*	*Gram.*	*Grams.*
0.2940	0.058	0.133	....	....	−0.129	0.1792
.5880	.366	.203	−0.109	0.321	− .100	.3192
1.176	.721	.403	.354	.500	.077	.5687
2.350	1.180	.880	.885	.954	.440	1.0650

Table VI contains data for Hagerstown loam, Marshall silt loam, and Norfolk sand. A correction for the volume of water absorbed on the soil grains was rejected here, as it amounts to less than 1 per cent, and the data serve to show the general trend of the distribution. As there is some organic matter already present in the soil, the absorption appears negative for low concentrations of manure extract, since the organic matter comes out of the soil and increases the total quantity present in solution. For Hagerstown loam the maximum absorptive capacity was found by extrapolation of the distribution curve to be approximately 1,700 parts per million. This means that with very great concentration of manure in solution 1 kilo of this soil would absorb 1.7 grams of soluble manure from the extract and no more. The data does not admit of calculating the maximum absorptive capacity for the other two soils, but a comparison of the soils on the basis of the highest quantity of manure absorbed by each gives a ratio of 2.7:2:1, in the order: Hagerstown loam, Marshall silt loam, and Norfolk sand. Here the order of the absorptive capacity is the reverse of that found for gentian violet as shown in Table IV, where Marshall silt loam had nearly twice the absorptive power found for the Hagerstown loam.

RELATION OF DISTRIBUTION TO THE USE OF FERTILIZERS.

This series of experiments is important in showing that absorption is dependent as much on the nature of the solute as on that of the absorbent. It further indicates the probable futility of attempting to select empirically a dye with which quantitative measurements might be made to determine the absorptive power of a soil for manures or fertilizers, or to determine its relative crop-producing power.

The experiments with gentian violet, together with those using manure, in Tables IV and VI, show that when fertilizers are applied to a soil relatively less and less soluble matter is absorbed from the fertilizer as more and more fertilizer is added to the same area. But on any given tract the *percentage* of fertilizer absorbed is greatest where the least fertilizer is used.

The usual application of fertilizers, however, does not raise the concentration of the soil solution appreciably. This is due to the fact that soils in the field can still absorb far more of the fertilizer constituents, and the conditions are represented by the steep portion of a distribution curve, in which region the soil absorbs large quantities of soluble material, leaving the solution very little different from the original soil solution.

Several of the cases given above for the distribution of a solute between water and soil can be represented by straight lines, that is, they can be described by a linear function of the form $C/C_1=K$. In what appears to be the more general type of distribution, however, the data do not accord well with the equation $C^n/C_1=K$, but with equations of a more complex form; in fact, for some distribution curves, when the logarithms of C and C_1 are taken and plotted, a curved line results, showing that *no exponential equation* describes this particular distribution curve. As these complex equations have no special significance and are purely empirical, they are not given here. One reason for these deviations from the simpler forms of the distribution equation was apparent in the marked changes in the state of aggregation or "flocculation"[a] of the soil particles induced by different concentrations of the solute in the aqueous solutions. In the absorption of eosine by quartz, where the distribution was nearly linear, there was no flocculation of the absorbing grains which could be observed; but the same quartz flour was flocculated when absorbing gentian violet, and very differently at different concentrations of dye. Moreover, the extent of the flocculation with increasing amount of dye went through a maximum, so that no simple formula could be expected to hold for the distribution curve. The soils studied showed similar flocculation phenomena. The foregoing data and considerations lead to the following conclusions:

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[a] Patten, Trans. Am. Electrochem. Soc. **10**, 67 (1906.)

(1) The distribution of solute between solvent and absorbent presents in general the same characteristics with soils as with other absorbents.

(2) For any series of soils or other absorbents the order of the absorptive capacities for one solute may be entirely different from the order for another solute.

(3) With one and the same soil or other absorbent the distribution function may be linear for one solute and asymptotic for another.

(4) Generally when soils are the absorbents the change of surface or "flocculation" introduces a modifying factor and the form of the distribution equation is rendered more complex.

EFFECT OF TEMPERATURE UPON DISTRIBUTION.

Biedermann[a] studied the effect of temperature upon absorption from solution. His results are not concordant, but are nevertheless what might have been expected when the effect of temperature upon humus and upon the various soil constituents, such as calcium carbonate, are considered. In general, for phosphates, the higher the temperature, up to 100° C., the greater the absorption, and after boiling for fifteen minutes still more solute was fixed by the soil. There are exceptions to this rule, where the absorption is less at higher temperatures; for potassium the absorption decreased with rise in temperature for five out of nine soils.

Bayliss[b] has further shown that the rate at which Congo-red is taken up by paper is accelerated by rise of temperature, but the total amount taken up when equilibrium is reached is less the higher the temperature; the temperature coefficient of the reaction velocity is very low, so that Nernst's theory as to the part taken by diffusion in heterogeneous reactions seems to apply to adsorption. At low temperatures, equilibrium is attained slowly; at room temperature, twenty-four hours is necessary. The adsorption complex of gelatine and inorganic electrolytes is also dissociated as the temperature rises, and no evidence of heat production in adsorption is obtained. The reaction between Congo-red and paper is reversible; so also is that between gelatine and electrolytes. It is, however, noticed that raising the temperature rapidly to 100° C. tends to fix Congo-red in paper.

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[a] Landw. Vers.-Stat., 11, 1 (1869).

[b] Biochem. Jour., 1, 175 (1906).

Draper and Wilson[a] have shown[b] that "bleu de nuit" may be absorbed by silk in two different manners, depending upon the temperature at which the dyeing takes place. Above 40° the dyed fabrics are much more resistant; at 15° the dyed fabrics "fade out" by a treatment with "soap solution" or with alcohol. When the temperature of the bath is raised, a part of the dye is fixed more firmly. These experiments have been extended to acid dyes. The silk dyed with anthracene red, acid 3B, employing 0.25 per cent of the dye in a solution of acetic acid, 0.2 per cent, offered a resistance to "soap solution" greater according to the temperature. If one makes the treatment with a solution of 1 per cent of neutral soap solution heated to 55° C. and allows an immersion of thirty minutes, the following results are obtained:

Table VII.—*Effect of temperature upon absorption according to Draper and Wilson.*

Temperature of the bath.	Dye remaining upon the absorbent.	Temperature of the bath.	Dye remaining upon the absorbent.
° C.	*Per cent.*	*° C.*	*Per cent.*
18.5	0.002	75	0.13
40	.01	90	.18
60	.11		

RATE OF ABSORPTION.

FORMULA EXPRESSING RATE OF ABSORPTION.

The simplest assumption that can be made is that the rate of absorption is proportional to the quantity of solute which the absorbent may yet take up; that is, to the difference between the specific absorptive capacity as defined on page 43 in this bulletin and the amount of solute already taken up. If in time t, the absorbent has taken up the amount of solute, y, while its specific absorptive capacity for a solution of that particular concentration is A, then the above assumption can be formulated thus:

$$\frac{dy}{dt}=K(A-y)$$

where K is the constant of proportionality for the particular absorbent and solution under standard conditions. In the following paragraphs a few typical cases will be described for various absorbents, including soils.

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[a] Jour. Soc. Chem. ind., 26, 667 (1907).

[b] Jour. Soc. Dyers and Colorists, 22, No. 9.

In testing this rate equation with the observed data, it will be more convenient to use the integrated form, namely,

$$\log (A-y) - Kt = \log A$$

which is a linear function with respect to $\log (A-y)$ and t. Since no special significance attaches to the constant K, Briggsian logarithms may be used for convenience. From inspection of this integrated equation it is evident that when the values $\log (A-y)$ are plotted against t a straight line results if the original differential equation, $\frac{dy}{dt} = K(A-y)$, correctly describes the rate of absorption.

EXPERIMENTAL TESTS OF FORMULA.

RATE OF ABSORPTION OF POTASSIUM BY A SOIL.

Peters[a] has determined the rate at which a soil absorbs potassium from an aqueous solution of potassium chloride. He does not give the temperature, but states that the experiments were carried out at Tharand in the summer of 1860 at room temperature. His results are given in Table VIII, where t represents the time in hours; y, the grams potassium oxide absorbed by 100 grams of soil; and $\log (A-y)$, the value calculated from A, 0.2168—the specific absorptive capacity of the soil for the end concentration of solution—less the value of y at each time given in the table under t.

When $\log (A-y)$ is plotted against t, the graph is not a straight line; and, in addition, $\log A$ as estimated by extrapolating the curve is less than the value of $\log A$ as found by experiment. Consequently it follows that the formula $\frac{dy}{dt} = K(A-y)$ does not describe the actual rate of absorption observed by Peters.

Table VIII.—*Rate of absorption of potassium oxide by a soil, according to C. Peters.*

[100 grams soil and 250 c. c. of 0.05 /N potassium chloride solution.]

Time.	K_2O absorbed $= y$.	$\text{Log}(A-y)$.	Time.	K_2O absorbed $= y$.	$\text{Log}(A-y)$.
Hours.	*Gram.*		*Hours.*	*Gram.*	
0.25	0.1417	$\bar{2}.814$	8	0.1860	$\bar{2}.499$
2	.1571	$\bar{2}.776$	24	.1990	$\bar{2}.251$
4	.1690	$\bar{2}.679$	48	.2168	....

RATE OF ABSORPTION OF OXALIC ACID BY ANIMAL CHARCOAL.

Lagergren[b] has determined the rate at which animal charcoal absorbs oxalic acid, and, using the reaction velocity equation of the first order $\frac{dy}{dt} = K(A-y)$, he has calculated a series of values of y, which are given together with those for t and y in Table IX. A is taken as the maximum quantity of oxalic acid absorbed. His calculated values do not agree with the experimental values of y sufficiently well to warrant the use of this equation.

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[a] Landw. Vers.-Stat., 2, 127 (1860).

[b] Bihang K. Sv. Vet. Akad. Handl., Band 24, Afd. II, No. 4, ii (1899).

TABLE IX.—*Rate of absorption of oxalic acid by charcoal, according to Lagergren.*

[Five grams charcoal and 10 c. c. of solution containing 4.241 grams oxalic acid per liter.]

Time, t.	y—oxalic acid absorbed.	Calculated value of y.	Time, t.	y—oxalic acid absorbed.	Calculated value of y.
Minutes.	*Gram.*	*Gram.*	*Minutes.*	*Gram.*	*Gram.*
5	0.046	0.042	180	0.245	....
10	.090	.076	360	.227	....
30	.151	.163	2,880	.249	....
60	.198	.215			

RATE OF ABSORPTION FROM PERCOLATING SOLUTIONS.

Schreiner and Failyer[a] have studied the rate at which phosphates and potassium are absorbed from solution passing through typical soils. A solution of definite concentration was percolated through soils, maintaining the rate of percolation constant by an automatic device, and determinations were made of the concentrations of solute, which increased in the successive percolates. It was found that each soil had its own specific absorbing power and that the process of absorption, considered as a volume rate, gave very regular curves when the quantity of phosphate absorbed was plotted against the total volume of solution which had been percolated. It was shown that the volume rate of absorption was well described by the differential equation

$$\frac{dy}{dv} = K(A-y)$$

where A is the "specific absorptive capacity" of the soil for phosphates in equilibrium with the solution, y is the quantity of phosphate which the soil has taken up from solution after v c. c. of that solution has passed through the soil, and K is a constant—the velocity constant. As the liquid passes from top to bottom each layer exerts its absorbing power upon weaker and weaker solution, and consequently the rate equation

$$\frac{dy}{dv} = K(A-y)$$

is a summation of all these various rates of absorption.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr. 1906; Jour. Phys. Chem., **10**, 239, 361 (1906). Compare Calugareanu and Henry, Compt. rend. Soc. Biol., **53**, 579 (1901). Diffusion of dye stuffs through gelatine.

RATE OF PERCOLATION THROUGH SOILS.

Seelheim[a] has examined quantitatively the factors which determine the rate of percolation through sand, clay, and calcium carbonate, and finds that Poiseuille's formula, $Q = C/L$, holds for all three solids. A mixture of two sands, one having grains small enough to lodge in the interstices between the grains of the other, gives very nearly (about 1.2 times greater) the percolation rate of the smaller grained sand. But where the two sands have grains more nearly of the same size, the percolation rate is the average of that for each sand separately. The rate of flow is directly proportional to the head of water and inversely to the thickness of the soil layer. Where several layers of soil are superposed, the speed of percolation is essentially that of the least permeable layer. The acceleration in flow due to increase in temperature was determined, and an interpolation formula, calculated by means of least squares, is given for the sand, clay, and chalk used.

RATE OF MOVEMENT OF LIQUIDS THROUGH CAPILLARY TUBES, AND THROUGH PAPER AND POROUS MEDIA.

The work of Cameron and Bell[b] on the rate of movement of liquids through capillary tubes and through paper and porous media gives a slightly different treatment of the rate of absorption during percolation. In their first paper an empirical equation was proposed to describe the movement of water and of aqueous solutions through blotting paper and through soils:

$$y^n = Kt$$

where y represents the distance through which the liquid has moved in the time, t, and n and K are constants depending upon the temperature and the specific substances. The second paper places this empirical equation upon a rational basis by deriving it from the formula of Poiseuille[c] for the movement of a liquid from one level to another through a capillary tube: $Q = C\frac{HD^4}{L}$ where Q is the quantity of liquid passed through in unit time; H is the difference in level, or "head;" D and L are the diameter and length of the tube, respectively; and C is a constant. This equation may be applied to the advance or retreat of water in a capillary tube only when the assumption is made that the energy gained or lost with change of velocity (the "velocity head") is negligible in comparison with the energy gained or lost in the change of level of the water or in the friction against the walls of the tube. This formula was found to hold very well for the movement of several pure solvents through capillary tubes.

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[a] Zeit. anal. Chem., **19**, 387 (1880).

[b] Bul. No. 30, p. 46, Bureau of Soils, U. S. Dept. of Agr. 1905; Jour. Phys. Chem., **10**, 658 (1906).

Ann. Chim. Phys. (3), **7**, 50 (1843).

Several series of experiments were made by Bell and Cameron using blotting paper and soils with water, aqueous potassium chloride solution, and aqueous sodium eosine, indigo-carmine, and coralline solutions, and the formula was found to hold in every case, with the restrictions that the acceleration be negligible in comparison with the velocity and that the length of the capillary soil tubes be great in comparison with their diameters. And, in addition, they have shown that this equation describes the movement through soils and paper of solutions which suffer change during the process. Both the advance of the solute and of water in the medium conform to this formula.

RELATION OF DISTRIBUTION TO RATE OF ABSORPTION FROM A PERCOLATING SOLUTION.

These rate-of-advance studies of Cameron and Bell are related to the percolation studies of Schreiner and Failyer. The latter maintained the rate of flow constant and plotted the total quantity of solute absorbed against the volume of solution percolated. It will require a long period of time to bring the lower layers of soil to anything like saturation with respect to the solute in question, so that throughout the percolation experiment there will be a different concentration of solution in contact with each layer of soil from top to bottom of the percolation tube.

The rate of selective advance in soils for indigo carmine and water through the Penn loam, for coralline and water through the Penn loam, and for coralline and water through the Podunk fine sandy loam shows that the advance of the dye is slower than that of the water, and is different for each dye. This means, of course, that the absorption effect exerted by the soil upon the solution robs it of nearly all the dye, until a point on the distribution curve is reached where the solution can retain sufficient dye to carry it along by percolation to the next layer of absorbent. Thus we are not in reality studying the rate of flow of the dye or of the dye solution in these experiments, but rather the retaining ability of the various absorbent materials for the dye as its solution percolates. When the absorbent material is fairly well saturated with the dye, the rate of flow will differ,[a] but not greatly, from that of water, save as the addition of distilled water changes the distribution and thus induces a flocculation or deflocculation of the grains of the absorbent, thus altering the channels in the soil and the diameters of the capillary soil tubes.

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[a] Krakow, Jour. Landw., **48**, 209 (1900), on comparing pure water and solutions side by side, found that the water moved more rapidly through a soil. Briggs and Lapham, Bul. No. 19, Bureau of Soils, U. S. Dept. Agr. 1902, p. 6, made the same observation, which they attribute to the greater viscosity of the solutions.

The absorption curves of Schreiner and Failyer are necessarily asymptotic, since the soil can absorb only a limited weight of salt from any given solution. Consequently their curves might be expected to fit some equation in which the dependent variable tends to a limiting value. This was found to be the case, the formula $\frac{dy}{dv} = K(A-y)$ serving remarkably well to describe their experimental results and others obtained in this laboratory.

The same consideration applies to the rate studies of absorption in general, viz, that there is a limit to the quantity which an absorbent can take up and retain under equilibrium conditions; therefore all curves plotted with quantity of substance absorbed as ordinate, y, and time of absorption, t, as abscissa, must necessarily tend to an upper limit for y. Consequently no exponential equation of the form $y^n = Kt$ can exactly describe absorption rate curves. For, when the time is infinite, the absorption, y, likewise is infinite; and this is contrary to experience.

Similarly in the rate-of-advance studies: The formula $y^n = Kt$ postulates that when $t = \infty$ the height of the liquid in the soil shall be infinite. This, again, is contrary to experience, the capillary water rising until its weight balances that of the capillary effect. But the formula was developed correctly enough for the advance or retreat of liquid in a horizontal capillary tube where y for all practical purposes is infinite, and the driving force, the capillary column of liquid, remains constant. With blotting paper, too, the formula was found to hold for short distances whether the paper was in a horizontal position with $y = \infty$; or held vertically with y approaching a limit. The application of this formula, then, to vertical columns of soil and blotting paper is justifiable, in that it enables us to handle and compare and analyze experimental data in a more satisfactory manner than by merely plotting the curves. But it should be borne in mind that the formula $y^n = Kt$ can not rigidly express any function which tends to a limiting value. This caution is emphasized here, since a number of rate curves are described by this formula for a limited range.

ENERGY CHANGES.

In general the treatment of energy change takes the form of measuring the change produced in properties of one substance by action upon it of a second. The energy in a body that is available for producing changes in another substance, or substances, other than heat is called the free energy. It is different at different temperatures, since the heat-capacity or energy-capacity of a body changes with the temperature.

When a body adsorbs another, one may expect several different energy changes, mainly—

(1) In cohesion and in surface energy.

(2) In work done on expansion or contraction of volume.

(3) Electrical effects; such as static charges on surfaces and upon suspended particles, and change in potential difference where metals are immersed in electrolytes.

(4) Heat effects; heat evolved or absorbed due to change in heat capacity, and due to a rearrangement of the whole system.

TEMPERATURE RISE CAUSED BY MOISTENING POWDERS.

Pouillet[a] observed a rise in temperature when various powders were moistened by different liquids using for this purpose—water, oil, alcohol, and ethyl acetate. As absorbents he used finely divided metals, metallic oxides, powdered glass, clay, and a number of organic substances.

A number of investigators have measured the rise in temperature occasioned by the absorption of various vapors by dry soils and other absorbents. A discussion with citations of this literature has recently been given,[b] and need not be repeated here.

CHANGE IN DENSITY OF ABSORBED LIQUIDS.

Hassenfratz[c] claimed that a substance such as glass after being powdered showed a smaller specific gravity than before, and that the adherence of air to the powder does not account for the phenomenon. But he gives one experiment *using the same sample of glass powder* in which the density obtained on weighing the glass under water in an evacuated flask was greater for the powdered glass than for the same glass in one sheet. Since this agrees with the results of later investigators, it is very likely that the other observations of Hassenfratz—where he found a lower density for the glass in powder form—were affected by incomplete removal of the absorbed gases from the glass. He has, however, shown very well by these experiments that a powder placed in a liquid and thoroughly stirred will retain a considerable quantity of gas, and that the last traces of this absorbed gas are very difficult to remove, even when the liquid containing the powder is placed in a vacuum.

In the case of water wetting a powder, Junk[d] found that above 4° C. there was an increase in temperature, and below 4° C. a decrease in temperature. This result is attributed to an increase in density at the surface of the powder, which above 4° C. would tend to increase the temperature of the mass of the liquid, and below 4° C. would decrease the temperature. Meissner,[a] however, has more recently found an increase in temperature at 0° C.

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[a] Ann. Chim. Phys., **20**, 141 (1822); Gilbert's Ann., **73**, 356 (1823).

[b] Bul. No. 51, Bureau of Soils, U. S. Dept. Agr.; Trans. Am. Electrochem. Soc. **11**. 387, 1907.

[c] Gilbert's Ann. **1**, 396 (1799).

[d] Pogg. Ann., **125**, 292 (1865).

ESTIMATION OF THE PRESSURE IN ADSORBED LIQUIDS.

Lagergren[b] has calculated the pressure of water at the surface of a solid consequent upon the increase in density, and finds a pressure upward of 6,000 atmospheres. Young[c] estimated its value for water at 23,000 atmospheres, while Lord Rayleigh[d] mentions with approval a hypothesis of Dupré, which leads to the value 25,000 atmospheres by a deduction from the dynamical equivalent of the latent heat of evaporation of water. A change in density has also been noted by Spring,[e] who found that the amount of water required to fill the spaces of a given mass of sand was greater than would be expected if it were merely a phenomenon of occupying the air spaces. This phenomenon has been ascribed to an increase in the density of the water at the surface.

TEMPERATURE INCREASE CAUSED BY MOISTENING SOILS.

Stellwaag[f] found the following increases in temperature by moistening soils and soil constituents with water: 8.33° C. for a calcium carbonate sand rich in humus; 6.6° C. for ferric hydroxide; 5.57° C. for a loam soil.

HEAT EVOLVED ON WETTING QUARTZ POWDER.

Martini[g] gives 13.73 calories as the heat evolved on wetting 1 gram of quartz powder with water. A mechanical analysis of the powder is not given. Similarly, charcoal evolved 14.45 calories per gram when placed in water. Ercolini[h] finds slightly different values: 13.23 calories for quartz, and 14.23 calories for charcoal.

HEAT EVOLVED ON WETTING CHARCOAL WITH VARIOUS LIQUIDS.

Martini[i] found each liquid has its own heat of wetting. Thus with granulated animal charcoal at 17°–18° C. water showed a rise in temperature of 15.58°; absolute ethyl alcohol, 17.47°; ethyl ether,

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[a] Wied. Ann., **29**, 114 (1886).

[b] Bihang. till K. sv. Vet.-Akad., Handl. 24, Afd. II, No. 5 (1898).

[c] Minchin, Hydrostatics and Elementary Hydrokinetics, 311 (1892).

[d] Phil. Mag., (5) **30**, 473 (1890).

[e] Mem. Soc. Geol. Belge, **17**, 13 (1903).

[f] Forsch. Geb. Agr. Phys., **5**, 211 (1882).

[g] Atti del R. Istituto Veneto (7) **9**, 958 (1897).

[h] Nuovo Cimento (4) **9**, 110 (1899).

[i] Atti del R. Istituto Veneto (7) **8**, 510 (1896).

17.50°; ethyl acetate, 18.94°; benzene, 17.60°; carbon disulphide, 20.60°. It is interesting to note, too, that benzene with impure charcoal gave no rise in temperature, and that amyl alcohol showed this same indifferent action, evolving no heat. Absolute alcohol caused a rise of 5.55° only, whereas less pure alcohol showed 10.03° rise. Unfortunately, data are not available for the conversion of these observations to calories.

Linebarger,[a] using the same sample of quartz powder with which Martini worked, found 13.80 calories evolved per gram when placed in water; 11.21 and 10.88 calories for nitrobenzene; 9.61 and 7.55 calories for toluene; 4.09 calories for benzene; 11.84 and 12.46 calories for pyridine. The granules of this powder had an average diameter of 0.0005 cm. Using another sample, with average diameter of grain, 0.00096, Linebarger found that practically half the quantity of heat given above for each liquid was evolved on wetting. He found, in common with previous investigators, that the relative quantity of liquid does not influence the heat effect. A certain minimum quantity of liquid is necessary to produce the maximum heat change, but any excess of that amount has no perceptible influence. The heat effect per unit mass of the powder is the same for the same liquid at the same temperature, provided this minimum amount be present.

HEAT EVOLVED BY POWDERS ON ABSORBING WATER VAPOR.

The experiments of Parks[b] indicate that the heat which water vapor liberates when it condenses upon the surface of the silica grains is returned to the liquid water (which is in the vessel with the silica to maintain the air space saturated with water vapor) as it evaporates to take the place of the water vapor which the silica had adsorbed. In the end, therefore, the same quantity of water is adsorbed and the same quantity of heat liberated when the silica is in contact with water vapor as when it is placed under liquid water.

PARKS'S LAW.

In another paper[c] Parks formulates a law, "When silica, sand, or glass is brought in contact with water, at approximately constant temperature, the heat evolved is proportional to the area of the surface exposed by the solid, and the amount of heat developed per square centimeter is approximately 0.00105 calorie when the temperature is near 7° C." And for a range of 17°, from 7° C. to 24.3° C., this heat evolution increases 0.0000035 calorie per square centimeter of surface for each degree increase in temperature. It has been suggested that this law of Parks's may be used to ascertain the area of a powder or a soil per gram by determining experimentally the heat evolved when the powder is placed in water and dividing this quantity of heat by the calories which 1 square centimeter of surface liberates when wetted. But here again we meet the same difficulty which confronted Kayser[a] in his attempt to determine the area of the surface presented by the grains of powder by measuring the quantity of water adsorbed by the powder and then dividing this weight of water by the number of grams of water adsorbed upon a surface of standard material. He failed to find a standard material. Each surface tried showed a different degree of adsorption. The researches quoted above show that each soil constitutent has its own heat effect when moistened; consequently, an attempt to measure the area of a soil in this manner is not promising.

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[a] Phys. Rev., **13**, 48 (1901).

[b] Phil. Mag. (6), **5**, 521 (1903).

[c] Phil. Mag. (6), **4**, 247 (1902).

In Linebarger's experiments[b] the heat evolved compared to the surface of silica exposed is greater than that shown by Parks. But in considering this apparent clash of results one must bear in mind that Linebarger has measured the heat effect of the same solid in different liquids and finds the ratio of the different heat effects for coarse and fine powder the same in different solvents. This is very strong evidence, indeed, that the heat evolved is proportional to the surface. The error involved in calculating the effective area of a powder is enormous. Parks's values involve the area as calculated from microscopic measurement of the granules. Linebarger's ratio is absolute, since he takes merely average samples of each grade of powder, without attempting to evaluate the area, and uses these two samples with each liquid.

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[a] Wied. Ann., **24**, 450 (1885).

[b] Phys. Rev., **13**, 48 (1901); see also:

Cantoni, Rend. del R. Istituto Lombardo, Class di Scienze Matematiche e Naturali, **3**, 135 (1866);
Martini, Atti del R. Istituto Veneto, (7) **8**, 502 (1896); (7) **9**, 727 (1897); (8) **2**, 615 (1900);
Tait, Proc. Roy. Soc. Edinb., **11**, 51 (1880–81); **11**, 813 (1881–82);
Marshall Smith and Omond, Ibid. **11**, 626 (1881–82);
Amagat, Compt. rend., **116**, 946 (1893);
Lussana, Nuovo Cimento (4) ii, 233 (1895);
Lagergren, Köngl. Vet. Akad. B. **24**, Afd. ii, Stockholm, (1899);
Tate, Phil. Mag. (4) **20**, 508 (1860);
Melsens, Mem. Acad. Belg., **23**, (1873); Ann. Chim. Phys. (5), **3**, 522 (1874);
Chappuis, Wied. Ann., **19**, 21 (1883);
Wiedemann and Lüdeking, Wied. Ann., **25**, 145 (1885);
Gore, Phil. Mag., **37**, 306 (1894); Birm. Phil. Soc. Proc., **9**, part 1, (1893).
Ercolini, Nuovo Cimento (4) **9**, 110 (1899);
Bellati, Atti del R. Istituto Veneto (8) **2**, 931 (1900);
Fitzgerald, Nature, **49**, 293, 316 (1894);
Weber, Pogg. Ann. 154, 367 (1875);
Barus, Phil. Mag. (6), **4**, 24, 262 (1902);
Magnus, Phil. Mag. (4), **6**, 336 (1853).

HEAT EVOLVED BY SWELLING STARCH.

Rodewald[a] has studied quantitatively the energy changes of starch as it absorbs water. One specimen evolved 24.02 calories per gram of starch; another, 19.4 calories. He finds that the greatest available effect in the passage of heat into work which can be reached in the swelling of starch is 11.4 per cent of the total heat effect, which latter is 24.02 calories. This result is based upon measurements of volume change during swelling. The average pressure between the ultramicroscopic cells of starch is calculated as 2,137 atmospheres, while very near to a cell wall the pressure would be much greater. Comparing this value with those of Dupré (25,000 atmospheres) and Young (23,000 atmospheres) and Lagergren (6,000 atmospheres), it seems probable that in the swelling of starch the imbibition effect predominates over the absorption.

COMPENSATING FACTORS THAT MASK THE ENERGY CHANGE IN ABSORPTION OF MATERIAL FROM SOLUTION.

The foregoing citations contain only the heat changes consequent upon the wetting of powders and the absorption of vapors. No values for the energy change accompanying absorption from solution are available, although it is possible to make such measurements. This phenomenon is analogous to the general problem of the energy changes attendant upon the process of solution. In this case the determinations of the individual forces at work is difficult; the actual heat and volume changes measured are the resultant of all the forces involved. Among these are the attraction of solvent and solute and the cohesion of the solute. Some idea of the cohesion of the solute may be obtained from its heat of vaporization. In like manner it is difficult to estimate the individual forces in the case of absorption from solutions, for there are the added factors of the attractions of the absorbent for both solvent and solute. At present the best indication of the magnitude of these forces is the chemical decomposition which they produce—decompositions which, effected in other ways, require large quantities of energy.

THE CONDITION OF THE ABSORBED SUBSTANCE.

THEORIES PROPOSED.

The earlier theories of absorption, and more especially of adsorption, were based either upon the assumption of a pressure at a surface layer of liquid higher than that in the free liquid or upon the theory of wetting of a solid by a liquid.

Only at the saturation point is it possible to consider the effect of pressure upon the solubility. The case of absorption from unsaturated solution must be considered as a distribution of the solute between layers of the liquid at different densities. This is analogous to the distribution of a solute between two different liquids or to the Soret effect, obtained when different portions of the solution are maintained at different temperatures, resulting in two solutions of different concentrations. The effect of pressures has been discussed by various authors.[a]

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[a] "Researches on the Swelling of Starch," Lipsius and Fischer, Leipsig, 1896.

From the principle of Le Chatelier[b] it follows that if on solution contraction occurs there will be a positive adsorption, i. e., the surface layers will become more concentrated.

A theory of absorption from solution has been based upon considerations of the surface tension between solid and liquid,[c] which tension there is no direct method of determining experimentally. It has, however, been derived from the theory of wetting of a solid by a liquid, and is shown to be less than the surface tension between solid and gas. In case the surface tension between solid and liquid is lowered by the addition of a substance soluble in the liquid, it follows that there will be adsorption of the substance on the surface of the solid, for the potential surface energy will tend to become lower by further concentration at the bounding surface.

PHYSICAL ABSORPTION.

Without entering deeply into the distinction between chemical and physical change, we may for practical purposes define a physical change as one in which the altered substance retains sufficient of its former characteristics to be recognizable as the same material present before the change took place.

On the basis of this definition we may classify a number of absorption reactions as physical changes, in that the dissolved substance as a whole is concentrated in the layer of liquid close to the absorbing solid, and in some cases even deposited upon its surface in a condition nearly or quite solid.[d] A good example of this is the adsorption of the organic dye gentian violet (gentianin) by quartz powder. Here the dye is retained in a thick layer upon the grains of quartz while the solution bathing the quartz is a thousand to ten thousand parts per million below its saturation point for this dye. Under the microscope the dye upon the quartz grains shows its characteristic colors for reflected and transmitted light, and when the dyed powder is subjected to percolation with distilled water the dye is gradually removed and recovered intact.[a]

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[a] Thomson, Applications of Dynamics to Physics and Chemistry, p. 237–240; Freundlich, Zeit. phys. Chem., **57**, 422 (1906); see also Lagergren, Bihang t. k. Sv. Vet. Akad. Handl., **24**, 2, No. 4 and 5 (1899); Parks, Phil. Mag (6) **4**, 240 (1902); (6) **5**, 517 (1903).

[b] See Bancroft, Phase Rule, p. 4 (1897).

[c] For references, see Freundlich, Zeit. phys. Chem., **57**, 421 (1906).

[d] Thomson, Applications of Dynamics to Physics and Chemistry, 1888, p. 91; Freundlich, Zeit. phys. Chem., **57**, 385 (1906); Ostwald, Lehrbuch der Allgemeine Chemie, (1891), p. 1096; Frank K. Cameron and James M. Bell, Bul. No. 30, Bureau of Soils, U. S. Dept. Agr. 1905.

In some cases the adsorbed material is retained in solution in the layer of liquid close to the surface of the solid. This is very well shown for alkaline carbonate solution with soil. The fine clay particles when suspended in the solution produce no appreciable lowering of the electrical conductivity, but when they are removed by centrifiugal action or by settling the quantity of adsorbed material which they carry down with them is sufficient to reduce the conductivity of the supernatant liquid to a marked degree.[b] And since these carbonates, or any chemical compounds they might form, have a low conductivity as solids it follows that they are present in solution at the surface of the soil particles and contribute to the conductivity of the main body of liquid in which the soil is suspended. Should the clay contain hydrated silica, alumina, or ferric oxide in an amorphous condition, part of the solution will be imbibed by them and removed when the suspension is cleared by settling; but in this case, too, the fact that the absorbed material contributes to the electrical conductivity shows that it is still in solution.

ABSORPTION BY CHEMICAL FIXATION.

In addition to these three types of physical absorption, we may have chemical fixation of dissolved bodies at the surface of a solid. The solute may be removed from solution as a whole and added to the solid absorbent to form a compound. Thus metallic silver will absorb chlorine from solution forming silver chloride. The absorbing solid, too, may lose some constituent at the same time that it absorbs the solute. Solid calcium hydroxide absorbs carbon dioxide from solution and loses water. Much more complicated replacement reactions between soil constituents and soil solution take place, as set forth at length in a previous bulletin.[c]

Since many cases of absorption are known in which both physical and chemical changes occur, the above classification, although convenient, should not be rigidly applied. Indeed, all gradations of union are possible, from purely physical surface adhesion—which still depends upon the composition of the bodies involved—to purely chemical combinations. One important intermediate step may be solution, either liquid or solid.

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[a] Trans. Am. Electrochem. Soc., **10**, 67 (1906).

[b] Electrochem. and Met. Ind. **5**, 257 (1907).

[c] Bul. No. 30, Bureau of Soils, U. S. Dept. Agr., 1905.

CALCULATION OF THE PROBABLE THICKNESS OF ADSORBED MATERIAL.

A series of calculations for several soils is presented in Table X. The concentration of gentian violet dye solution at the surface of soil grains is estimated from the quantity of hygroscopic water and from the quantity of dye absorbed by the soil. This involves the assumption that the hygroscopic water determined by allowing dried soil (110° C.) to take up moisture from a saturated atmosphere is the same in quantity as the moisture retained upon the soil grains when the soil is in a saturated condition.[a] The results not only show the magnitude of the surface concentration, but also are of value in studying the physical condition of soils.

TABLE X.—*Relation of gentian violet dye absorbed to area of soil and to hygroscopic water.*

Soil.	Dye absorbed per 100 grams soil.	Hygroscopic water per 100 grams soil.	Dye in solution on soil grains.	Volume of solution retained by 100 grams of soil.	Area of soil per gram.
	Grams.	*Grams.*	*Per cent.*	*C. c.*	*Sq. cm.*
Marshall silt loam	0.3	4.0	7.0	....	2,320
	.485	4.0	10.8	47	....
	.9999	4.0	20.0	50	....
	1.50	4.0	27.3	47	....
	1.999	4.0	33.3	....	....
	2.497	4.0	38.4	....	....
	2.991	4.0	42.8	....	....
	3.119	4.0	43.8	....	....
	3.70	4.0	48.1	....	....
Hagerstown loam	.0	4.5	....	61	....
	.20	4.5	4.3	56	2,270
	.4	4.5	8.2	54	....
	.5	4.5	10.0	55	....
	.998	4.5	18.1	57	....
	1.495	4.5	25.0	50	....
	1.981	4.5	30.6	45	....
	2.045	4.5	31.3	....	....
	2.025	4.5	31.0	....	....
Quartz flour	.000	.8	....	36.5	1,260
	.019	.8	2.32	36	....
	.038	.8	4.53	38	....
	.075	.8	8.58	48	....
	.098	.8	10.90	50	....
	.190	.8	19.20	46	....
	.265	.8	25.0	40	....
	.289	.8	26.52	37	....
	.295	.8	26.93	34	....
	.297	.8	27.03	30	....
	.293	.8	26.80	29	....

Gentian violet is not very soluble in water, a 2 per cent solution being viscous and 6.81 per cent its solubility at 25° C.; yet the calculated per cent of dye in solution on the soil grains is 48.1 for Marshall silt loam, 31 for Hagerstown loam, and 27 for quartz flour. Although the hygroscopic moisture held by the quartz is less than one-fifth of that of the Hagerstown loam, the percentages are in very close agreement. The percentage of dye held in solution is actually higher than these values given, since the dye absorbed is in or on the soil grains, while part of the hygroscopic water should be reckoned as capillary water and is the same in concentration as the supernatant solution from which the dyed soil grains have settled out.

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[a] Parks, Phil. Mag. (6), 5, 521 (1903).

Since the calculation just made gives such high values for the concentration of dye upon the soil grains, it may even be that the dye is not in solution in the surface layer, but has separated upon the grains as a solid. The work of Rohde[a] is in line with this. He states that the aqueous solutions of fuchsine and methyl violet form at their surfaces solid layers which through their metallic luster are unmistakably evident to the eye. The surface of the liquid becomes first more concentrated, then viscous, and finally stiff and solid, so that in the condition of equilibrium the solution is covered with a skin of solid dyestuff.[b]

Rohde says, again, that the solid surface layer is the thicker and forms the faster the more concentrated the solution. According to his calculations the thickness of the layer (of solid dye) is always of a lower order of magnitude than the radius of the sphere of action. The present calculation, however, shows that the layer of dye on the grains of quartz flour, Marshall silt loam, and Hagerstown loam is many fold that of the calculated molecular dimensions. This is also true for the absorbed layer of eosin and for manure extract, and aside from these calculations microscopic examination shows a very appreciable layer of dye on the grains.

EFFECT OF ABSORPTION UPON THE PHYSICAL CONDITION OF THE SOIL.

RELATION OF ABSORPTION TO THE FORMATION OF AGGREGATES.

The absorption of nutrient salts by the soil not only maintains a proper soil solution, but also exercises a marked influence upon the size of the soil aggregates. This soil structure in turn governs the water-holding power, the porosity, and consequently the aeration of the soil; and these factors are of the utmost importance to the bacterial life in the soil, as well as to the changes in the organic and mineral constituents. The effect of absorption upon the soil solution has been discussed in several preceding chapters.

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[a] Ann. Phys., **19**, 935 (1906); see also the references given in the preceding sections.

[b] “Es spricht nichts gegen die Annahme, dass die molekularen Kräfte, welche die Ausscheidung des festen Farbstoffs bewirken, dieselben sind, wie bei der Oberflächenspannung der Flüssigkeiten tätigen. Es Würden namlich die grossen zwischen zwei Wasser moleküln wirkenden Kräfte, welche auch die grosse Oberflächenspannung des Wassers zur Folge haben, es bewirken müssen, dass die an der Oberfläche der Farbstoffslösungen befindlichen Farbstoffmoleküle, mit frosserer Kraft in das innere der Lösung gezogen werden, als die dort befindlichen Farbstoffmoleküle, was die bobachtete Anreicherung der Oberfläche an Farbstoff zur unmittelbaren Folge ergibt.”

The present chapter has to do with the changes in the physical structure of the soil attendant upon the addition of various soluble substances, such as fertilizers and correctives and salt water from inundations. When a salt is absorbed by a soil in suspension, there may occur either the formation of larger aggregates or else the breaking up of aggregates already present. Larger aggregates settle more readily and occupy a larger volume, while the smaller aggregates or single grains settle much more slowly and into a compact bed.

The direct relationship between the absorption of soluble material by percolates in suspension and their settling has been shown by Linder and Picton,[a] as well as by Whitney and Ober.[b] Colloids which settle from suspension in neutral solution carry down small quantities of metallic hydroxides.

Several hypotheses have been advanced to account for the formation and breaking up of aggregates.

Many of the agents which produce flocculation have been found to be more or less hydrolyzed in aqueous solution, and the flocculating power has been attributed to this hydrolysis. Freundlich[c], however, has found that the flocculating power of barium salts, which are scarcely hydrolyzed, is almost equivalent to that of beryllium salts and uranyl nitrate, both of which are strongly hydrolyzed, and as all of these salts have bivalent cations this can not be attributed satisfactorily to the difference in valence.

Another theory growing out of their work attributes the precipitation of suspended particles to the ions of the salt in solution. The mechanism of this precipitation is such as to constitute the neutralization of the charge of electricity upon the suspended particles by the ions carrying the opposite charge. On the basis of their experiment, in which they used electrolytes and nonelectrolytes, it has been claimed by Barus,[d] Bodländer,[e] Freundlich,[f] and Whitney and Ober[g] that the power to flocculate colloids is possessed exclusively by electrolytes.[h]

The flocculation of colloids by electrolytes has been investigated by Schulze,[i] Hardy,[j] and many others, and there has been a tendency to correlate the flocculating power of an ion with its valence. Schulze found that the power of salts of univalent, bivalent, and trivalent metals to flocculate colloids was in the proportion of 1 to 30 to 1,650. This in turn has been ascribed by Bredig[a] and Spring[b] to the hydrolysis of the salt, the degree of which increases very rapidly as the valence of the cation increases.

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[a] Jour. Chem. Soc., **67**, 63 (1895).

[b] Jour. Am. Chem. Soc., **23**, 842 (1901); Zeit. phys. Chem., **33**, 385 (1901).

[c] Zeit. phys. Chem., **44**, 129 (1903).

[d] Am. Jour. Sci., **37**, 122 (1889).

[e] Nach. K. Ges. Wiss., Göttingen, 1893, p. 267.

[f] Zeit. phys. Chem., **44**, 136 (1903).

[g] Jour. Am. Chem. Soc., **23**, 842 (1901); Zeit. phys. Chem., **33**, 385 (1901).

[h] Compare, Kahlenberg, Jour. Phys. Chem. **6**, 1 (1902); **10**, 593 (1906).

[i] Jour. prakt. Chem. **133**, 431 (1882); **135**, 320 (1883).

[j] Proc. Roy. Soc., **66**, 111 (1900); Zeit. phys. Chem., **33**, 385 (1901).

Colloid suspensions have been divided into two classes: Those which migrate toward the cathode under electrical stress and those which migrate toward the anode. The colloids which migrate toward the anode are said to be precipitated by anions, and vice versa. This migration of the colloids resembles the behavior of an electrolyte, and the theory has been advanced that colloids in solution are in reality large aggregations with small electrical charges,[c] which are counterbalanced by the presence of ions carrying the opposite charge. Thus there would be an equilibrium between the two, and a disturbance of the equilibrium by the addition of a salt to the solution tends to precipitate the colloid. Further, both classes of colloidal suspensions have the peculiarity that any one is precipitated from the solution when added to a suspension of one of the other classes, the precipitate being of course a mixture of the two.[d]

Hilgard[e] has shown that increase of temperature decreases flocculation; alcohol and ether decrease flocculation, as do also alkalies, while neutral salts, acid, and lime promote flocculation. Whitney[f] has also given considerable attention to flocculation, especially its effect upon the adaptation of special crops to soils. At his suggestion Bliss[g] made a study of the precipitation of suspensions and found that sodium chloride and hydrochloric acid induced flocculation, while potash and ammonia inhibited it, and also that the concentration of the solution is a determining factor. Bodländer[h] has given the concentration of typical acids, bases, and salts required to precipitate kaolin suspended in water. Sachsse and Becker[i] have determined the percentage of several salts precipitated from suspension by lime water.

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[a] Anorganische Fermente, 1901, p. 15.

[b] Bul. Acad. Roy. Belg., 1900, 483.

[c] Duclaux, (Compt. rend., **140**, 1544 (1905)) considers the granules of a colloidal solution as of such magnitude that they may be regarded as conductors of electricity.

[d] Linder and Picton, Jour. Chem. Soc., **67**, 63 (1895); Freundlich, Zeit. phys. Chem., **44**, 129 (1903); des Bancels, Compt. rend., **140**, 1647 (1905).

[e] Forsch. Geb. Agr. Phys., **2**, 441 (1879); also Silliman's Jour., **17**, March, 1879: ibid, **6**, Oct. and Nov., 1873: See also S. W. Johnson, Rept. Conn. State Board Agr., 1877–1878, Hartford, 1878, The reasons for Tillage.

[f] Bul. No. 5, Division of Agricultural soils, U. S. Dept. Agr., 1896, p. 9; Fourth Annual Report, Maryland Exp. Sta., 1891, p. 258; Bul. No. 4, Weather Bureau, U. S. Dept. Agr. (1892), p. 80; See also Wiley, Principles and Practices of Agricultural Analysis I, 1894, p. 171.

[g] Phys. Rev., **2**, 241 (1895).

[h] Neues Jahrb. f. Mineral. II, p. 147, 1893; abstr., Forsch. Geb. Agr. Phys., **18**, 76 (1895).

[i] Landw. Vers.-Stat., **45**, 137 (1894); abstr., Forsch. Geb. Agr. Phys., **18**, 78 (1895).

Matthews[a] has suggested that the precipitation of colloids by electrolytes is brought about by an alteration in the surface energy of the colloid. The suspending power of the solvent has been correlated with its dielectric constant. Buckingham,[b] however, has shown experimentally that this suspending power, while parallel with the dielectric constant, shows variations of a totally different order of magnitude. Many cases are known in which the flocculation and suspension of particles, bacteria, etc., alternate as the concentration of the solute is increased.[c] This recurrence of flocculation and suspension[d] puts in doubt the hypothesis that suspended particles settle because their charges are neutralized by the ions about them. Buxton and Shaffer[e] have suggested that this precipitation may be analogous to the phenomenon of "salting out," in which a new distribution of the components between solid and liquid phases in the colloidal suspension takes place. In other papers Teague and Buxton[f] have investigated the migration of suspended particles under the influence of electrical stress and found that the direction in which the suspension migrates depends upon the concentration of the electrolyte, and, indeed, alternates as the suspension or flocculation alternates. They suggest the possibility that this alternation may be due to a decrease in the absorptive power of the suspended particles in more concentrated solutions.

Hilgard has given considerable attention to the subject of sedimentation, especially in his method for the mechanical analysis of soils. He has also studied the effect of different salts, alkalies, and acids upon the physical structure of the soil, recognizing the effect of these agents upon sedimentation. His latest statement concerning the formation of soil crumbs is of interest: "When land is plowed in the proper moisture condition, the crumbs or floccules are held together by the surface tension of the capillary films (menisci) of water at the points of contact. In the case of sands, the crumbs will collapse into single grains whenever the water films evaporate, unless some cementing substance was dissolved or suspended in the water. Lime carbonate is one of the substances most commonly found permanently cementing the floccules; hence the ready tillage of most calcareous soils, and especially the loose texture of the 'loess' of the western United States and of Europe and Asia. In these deposits we find sandy and silt aggregates or concretions ranging from 10 or more inches in length (loess puppets) to microscopic size, held together by lime carbonate, but collapsing into silt and sand when the material is treated with acid so as to dissolve the cement. The rough surface of these aggregates, gripping into each other, explains the stability of the steep loess cliffs in the United States, as well as in northeastern China, as observed by Von Richtofen and Pumpelly." [a]

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[a] Am. Jour. Physiol., **14**, 203 (1905).

[b] Trans. Am. Elec.-Chem. Soc., **9**, 261 (1906).

[c] Bechhold, Zeit. phys. Chem., **48**, 385 (1904).

[d] With regard to the protecting action of gelatine and other substances upon the colloidal suspensions, reference may be made to Bredig, Anorganische Fermente (1901).

[e] Zeit. phys. Chem., **57**, 47 (1906).

[f] Ibid., **57**, 64, 76 (1906); **60**, 469, 489 (1907); **62**, 287 (1908).

Mayer,[b] starting from the well-known settling of muddy water by addition of common salt, divides the salt solutions into two classes: (1) those which behave like distilled water, allowing the soil particles to settle regularly according to their diameters and specific gravities; (2) those solutions in which the precipitate forms a mass of cohering flocs, the neighboring particles showing a tendency to hold together. He places hydrochloric acid, nitric acid, sulphuric acid, their salts, fixed alkalies (NaOH, KOH, LiOH), and ammonia in the first class. Alkali sulphates have only a slight tendency to promote sedimentation. Lime water precipitates the suspension of soil even better than fixed alkalies, while powdered calcium carbonate mixed with the soil before stirring with water has no effect upon the rate of settling.

Mayer also showed that sedimentation is not perceptibly affected until the concentration of solution added reaches a fairly definite per cent. The percentages at which precipitation just takes place are for the following solutes: Soap, 2.5; ammonia, 2.5; neutral sodium phosphate, 2.0; phosphoric acid, 0.8; potassium hydroxide, 0.56; sodium sulphate, 0.4; calcium hydroxide, 0.08; sulphuric acid, 0.025. The soil used was a fine clay from Iowa washed free of carbonates by hydrochloric acid. He showed that a soil subjected to percolation by distilled water at constant pressure allows the liquid to pass through at a constantly decreasing rate. This decrease is produced by packing and by clay particles lodging in the minute soil channels. When a salt solution belonging to his second class—i. e., one capable of precipitating the soil from suspension in water—is passed through a soil already washed and well packed down by percolation, an increase in the rate of flow is observed. He confirmed this phenomenon for sodium chloride and calcium hydroxide and, furthermore, showed that on washing out by percolation the salt absorbed by the soil during its contact with salt solution the rate of flow was very greatly reduced. This phenomenon has been fully confirmed in this laboratory[c] for potassium carbonate solutions passing through Galveston clay, Marshall silt loam, Hagerstown loam, and

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[a] Hilgard, Soils, p. 110 (1906).

[b] Forsch. Geb. Agr. Phys., **2**, 251 (1879).

[c] See page 94; also Cameron and Patten, Jour. Am. Chem. Soc., **28**, 1645 (1906); also Hissink, Chem. Weekblad, **4**, 663 (1907).

Norfolk sand. As a practical application of this sedimentation effect produced by salts, Mayer suggests first that lands flooded by sea water may suffer a deterioration in their physical condition on being again drained. This close packing of the soil would be likely to appear in the second year after flooding rather than in the first. He thinks, too, that the packing of the soil and consequent reduction of air space and ventilation facilitates the reduction of iron sulphate to hydrogen sulphide, or its analogues, especially in alkali soils. As land flooded by sea water, and thus put into dense condition, was not improved by use of lime, he suggests as a last resort that the land be left fallow, subject to freezing and thawing and to the action of turned-under green manure, such as natural plant growth. He points out most strongly the injury to the mechanical structure of a soil rich in clay produced by repeated fertilizing with potassium nitrate. A soil forced in this manner at first gives fine crops, then shows a sudden drop, which can not be corrected by simple addition of all the standard fertilizers. The soil is ruined mechanically for a long time. One of the reasons for this is that the nitrates, like the chlorides, are comparatively easily washed from the soil, and the salt being removed the soil grains pack down in a single-grain condition very hard to overcome. Swaving[a] likewise found that soils flooded by sea water were greatly injured in their physical condition, although not enough salt was absorbed to injure plants.

Fickendey[b] states that the precipitation of a suspension of a natural clay soil requires a much higher concentration of alkalies than is necessary to flocculate a kaolin suspension. He explains this as due to the protective action exercised upon the soil particles by the humic acids which go into the solution when the soil is treated with alkalies and alkali carbonates. Artificial humic acids can likewise restrain precipitation, though less strongly than the humus products of the soil. Tannin also prevents sedimentation, while starch has no perceptible effect. Pure gelatine without addition of electrolyte exerts a precipitating effect upon kaolin suspensions, which increases with the gelatine concentration up to a maximum and then drops considerably. Addition of alkalies to the gelatine solution displaces this maximum speed of settling toward the side of low gelatine concentration; but in acid solution this maximum appears nearer the region of concentrated gelatine solutions and is sharply defined. These observations are taken as giving new light upon the manurial efficiency of lime, in that it precipitates the humic acids of the soil, thus removing substances which tend to maintain the soil in a single grain condition, and enables the soil grains to flocculate and assume open physical condition.

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[a] Landw. Vers.-Stat., **51**, 463 (1898-99).

[b] Jour. Landw., **54**, 343 (1906).

EFFECT OF ABSORPTION UPON WATER-HOLDING POWER OF SOILS.

Van Bemmelen[a] and others have set forth the relation between the absorptive power of a finely divided solid and the quantity of water retained by the individual particles within their own bodies. But in addition to this imbibition effect, soluble material held in concentrated form upon the surface of powder grains materially alters the quantity of solution which this powder can retain in the space between grains after settling from suspension in the given solution.

Wollny[b] has shown that from every standpoint the single grain soil is inferior to a flocculated soil as regards its moisture content and conservation, as well as in respect to aeration.

Ulreich[c] gives data on the influence of various hydroxides, carbonates, phosphates, sulphates, nitrates, and chlorides upon the water content of soils. He concludes from his data that the different hydroxides and salts, in a considerable degree, but in different direction, exercise an influence upon the water-retaining power of the soil. According to their action they may be brought into three groups, of which the first comprises those compounds which produce a lowering of the water capacity of the soil, i. e., hydroxides and carbonates of the alkalies as well as phosphates. A second group includes those salts which appear to be almost without influence upon the retention of water; these are the sulphates. In a third class are the compounds such as nitrates, chlorides, and calcium hydroxide, which increase the water capacity of the soil. He also compares the effect of Knop's nutrient solution[d] with that of lime and obtains similar results with all the soils tried. The Knop solution increased the water capacity of the soil, as would be expected from the preponderance of nitrates and chlorides. This effect is greater as the concentration of the solution increases, so far as his experimental data go, save in the case of gypsum, where the soil held the same volume of solution at 0.1 per cent $CaSO_4$ as at 0.5 per cent, and showed a very slight decrease in water content when a 1 per cent solution was used.

The interdependence of absorption, flocculation, and physical condition of soils is shown in a series of preliminary experiments carried out by Mr. J. O. Belz. The quantity of solute retained in the soil spaces after settling from a given solution was determined by measuring the height of the soil surface. Since the true volume of the soil grains is a constant, the volume of water held in the capillary spaces may be calculated from this height. Susquehanna clay appears to retain a maximum volume of liquid in potassium hydroxide solution when the concentration is near 0.01 N. This same soil retains more of 0.1 N ammonia solution than of other concentrations used. In both these cases the definite location of the concentration giving maximum open structure remains to be determined, but its existence is assured. With sulphuric acid the volume of solution in the pore spaces is greater as the concentration of acid in solution increases up to 0.1 N, the strongest solution used. Susquehanna clay and quartz flour retain less of distilled water in their capillary spaces than of solution, while Hagerstown loam holds more of distilled water—which, of course, becomes a soil solution proper to that soil—than of dye solution; yet this soil, too, shows a maximum after the first quantities of dye have been absorbed. Calcium nitrate solution (200 c. c.) was shaken up with 25 grams of Sharkey clay and allowed to settle three days before taking the reading. The clay retained a greater volume of the 0.01 N solution than of the other solutions higher and lower in concentration.

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[a] Zeit. anorg. Chem., **23**, 112 (1900).

[b] Forsch. Geb. Agr. Phys., **16**, 406 (1893); **18**, 63 (1895); Puchner, Ibid., **19**, 1 (1896).

[c] Ibid., **19**, 52 (1896).

[d] This solution contains KH_2PO_4, $MgSO_4$, KNO_3, NH_4Cl, in equal parts by weight, with 4 parts $Ca(NO_3)_2$.

Table XI gives the results of a number of experiments also carried out by Mr. Belz. The solutions used were 0.5 and 0.1 normal, except lime, where the concentration was calculated on a basis of pounds per acre. Fifty grams of Susquehanna clay were shaken up with 150 c. c. of solution and allowed seven days in which to come to equilibrium. The results show that the solute used, and in particular its concentration in the soil and in the solution, determines the volume of solution which the soil can retain in its capillary spaces. It is to be remembered that the original concentrations given in Table XI have changed, since in each case the soil has abstracted a goodly quantity of solute from the solution.

TABLE XI.—*Volume of solution retained by Susquehanna clay on settling from various solutions.*

[50 grs. soil+150 c. c. solution.]

Solute.	(1) Volume of solution in soil.[a]	(2) Volume of solution in soil.	(1) Difference in volume over distilled water check.	(2) Difference in volume over distilled water check.
	0.5 normal solution.	0.1 normal solution.		
	C. c.	*C. c.*	*C. c.*	*C. c.*
Distilled water	75.4			
Lime (1)	72.0		−3.4	
Lime (2)	59.1		−16.3	
$(NH_4)_2CO_3$	104.6	105.6	29.2	30.2
K_2CO_3	91.4	126.4	16.0	51.0
Na_2CO_3	128.1	131.9	53.2	66.5
H_2SO_4	120.9	101.2	45.5	25.8
K_2SO_4	110.4	117.7	35.0	42.3
Na_2SO_4	126.1	113.8	50.7	38.4
$(NH_4)_2SO_4$	111.3	117.6	35.9	42.2
Na_2HPO_4	126.7	128.7	51.3	53.3
$(NH_4)_2HPO_4$	118.1	125.8	42.7	50.4
K_2HPO_4	108.7	123.2	33.3	47.8
$Ca(NO_3)_2$	60.5	69.4	−14.9	−6.0
$NaNO_3$	97.7	69.8	22.3	−5.6
KNO_3	80.4	70.1	5.0	−5.3
$(NH_4)NO_3$	73.0	89.4	7.6	14.0

[a] The volume of the air-dry soil is 41.1 c. c. for 50 grams.

Column 1=1,000 pounds per acre. Column 2=500 pounds per acre.

Increase in lime increases the volume of solution in the soil, and the same is true for sodium, potassium, and ammonium nitrates, sulphuric acid, and sodium sulphate; but the other salts studied show the reverse, the volume of solution retained by the soil being greater for lower concentrations. This apparent lack of agreement of the effect of various solutes is due to the fact that each solution has its own particular concentration for which the soil in contact with it will assume a maximum open structure.

The following experiments were undertaken to establish a relationship between the quantity of substance absorbed by the particles and the volume of solution which they can retain in the spaces between particles when the aggregate of grains is allowed to settle out of solution and pack down. Consequently in addition to determining the concentration of the solution remaining above the quartz flour, as shown in Table IV, its volume was measured; that is, the volume of liquid which could be drained off from the quartz after the bottles containing the system had been centrifuged at high speed for about ten hours and then allowed to stand some six weeks upon the shelf. As the quartz had settled into a compact mass in every bottle, the volume of liquid remaining above the quartz could be poured off cleanly and measured to within less than 0.3 c. c. The water added to each sample of quartz may be considered to be in three conditions—absorbed water, that held in the capillary spaces, and free water. The free water was directly determined, and the absorbed water has been determined for the same samples of quartz;[a] consequently the water held in the capillary spaces may be estimated by difference.

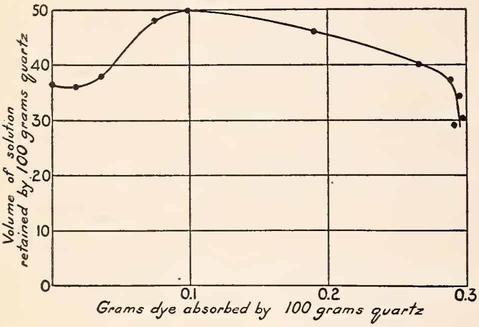

FIG. 2.—Curve showing the relation of the quantity of gentian violet dye absorbed by quartz flour to the volume of solution retained by the quartz after settling.

Table XII shows the volume of solution retained in the capillary spaces of 100 grams of quartz flour for different quantities of gentian violet dye absorbed by the quartz grains.[b] The corresponding concentration of each dye solution used has been given above in Table IV. The curve given in figure 2 is plotted from Table XII, using the grams of dye absorbed by 100 grams of quartz flour as abscissas and the volume of solution retained by the quartz in the capillary spaces as ordinates. The maximum of liquid is held by the quartz between its particles when about one-third of the dye which can be taken up by the grains has been adsorbed.

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[a] Patten and Gallagher, Bul. No. 51, Bureau of Soils, U. S. Dept. Agr., 1907.

[b] Trans. Am. Electrochem. Soc., **10**, 67 (1906).

TABLE XII.—*Volume of solution in the capillary spaces of quartz flour when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.	Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.	Dye absorbed by 100 grams of the quartz flour.	Volume of solution retained by 100 grams quartz flour.
Gram.	*C. c.*	*Gram.*	*C. c.*	*Gram.*	*C. c.*
0.000	36.5	0.0984	50	0.295	34
.017	36	.1901	46	.297	30
.036	38	.266	40	.293	29
.074	48	.289	37	.290	29

Similar measurements, using Hagerstown loam soil, are given in Table XIII. The maximum pore space for this soil evidently is attained with no dye present, and as the quantity of dye absorbed by the soil grains increases the soil settles together and retains less and less liquid, then expands again as it takes on more dye, till when 1 gram of dye is absorbed by 100 grams of soil, 57 c.c. of solution remains in the pore spaces. Further increase in the dye absorbed decreases the volume of solution in the capillary spaces. With 2 grams of dye to 100 grams of soil 45 c.c. of solution is held. This is 26.2 per cent less capillary liquid than the undyed soil retained, and 21 per cent less than is held by the soil containing 1 gram absorbed dye per 100 grams of soil. Marshall silt loam also shows this same volume effect, as indicated by the data in Table XIV.

TABLE XIII.—*Volume of solution in the capillary spaces of Hagerstown loam when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.	Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.
Gram.	*C. c.*	*Grams.*	*C. c.*
0.0	61	1.0	57
.20	56	1.495	50
.40	54	1.98	45
.60	55		

TABLE XIV.—*Volume of solution in the capillary spaces of Marshall silt loam when various quantities of gentian violet have been absorbed.*

Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.	Dye absorbed by 100 grams soil.	Volume of solution retained by 100 grams soil.
Grams.	*C. c.*	*Grams.*	*C. c.*
0.50	47	3.7+	39
1.00	50	3.7+	37
1.50	47		

TABLE XV.—*Volume of solution in the capillary spaces of quartz when various quantities of eosine have been absorbed.*

Eosine absorbed by 100 grams quartz.	Volume of solution retained by 100 grams.	Eosine absorbed by 100 grams quartz.	Volume of solution retained by 100 grams.
Gram.	*C. c.*	*Gram.*	*C. c.*
0.00000	42	0.0348	29
.00135	30	.42	29

The effect of eosine dye upon the volume of solution which quartz flour can retain in its capillary space serves to further correlate flocculation and absorption with the physical condition of a soil. Considering the data given in Table XV, we see that the absorption of 0.00135 per cent of the dye reduces the volume of liquid retained from 42 c. c. to 30 c. c. and that further absorption of dye has very little effect upon the volume of liquid in the pore spaces. Turning back to Table XII and figure 2, it appears that this volume, 30 c. c., is the same as the lowest volume of liquid held by 100 grams of quartz flour when its absorption capacity for gentian violet is reached. These suspensions of quartz flour in eosine solution were allowed to settle for over five weeks, and when the supernatant liquid was poured off in each case quartz particles were still suspended in the liquid, although the bottles had been subjected to rapid centrifugal treatment for two days at the beginning of this period. The volume of quartz flour not yet settled from the eosine solutions was insufficient to affect the accuracy of the measurements on the volume of solution retained by the compact mass of quartz at the bottom of each bottle. It shows, however, that the eosine dye had deflocculated the quartz particles and that the smallness of the volume of solution, 30 c. c., retained by the settled quartz flour is in all likelihood due to the fact that these particles settled from suspension as single grains or in small aggregates, i. e., deflocculated. The quartz suspensions in gentian violet solution were very noticeably flocculated, save for the high concentrations, where long-continued centrifuging was necessary to clear the solution of suspended quartz particles. And reference to figure 2 will show that the volumes of dye solution retained by quartz are parallel to the condition of the system as regards flocculation, the small volume, 30 c. c., being held by quartz when the concentration of the solution in gentian violet dye is high.

It is evident, then, that the quantity of soluble material absorbed by a soil has a marked influence upon the arrangement of the soil grains into aggregates. Different salts have widely different effects upon the soil structure, and the particular strength of soil solution for which the formation of soil aggregates is a maximum is not the same for each salt. Consequently where mixed solutions, such as those which exist in soils under field conditions, are used it will require a vast deal of experimental work before a prediction can be made as to the exact effect of a particular solution upon the physical condition of a soil.

Nevertheless the above treatment of the effect of absorbed material upon the physical condition gives a good understanding of the agencies at work in the formation of soil structures. And when this point of view is coupled with definite data, such as that in Tables XI to XV, the probable effect of a fertilizer or corrective upon the physical condition of a soil may be given, as well as its addition of mineral plant nutrients. This is especially needed since some fertilizers rich in mineral plant nutrients are ultimately injurious to the physical condition of a soil in a very high degree.

PERCOLATION STUDIES.

RECLAMATION OF BLACK ALKALI SOIL BY LEACHING.

The reclamation of soils containing "black alkali," or soluble carbonates, presents unusual difficulties. These difficulties are due in large part to the fact that soils generally show decidedly higher absorptive powers toward bases present in alkaline solutions than when the solutions are neutral or acid,[a] and that the presence of hydroxides or carbonates of the alkalies frequently induces a "puddling" of the soil, preventing a thorough penetration by water and subsequent removal of the water, with its dissolved contents, by drainage. The latter effect was subjected to a laboratory investigation by Cameron and Patten,[b] using two "black alkali" soils which were in process of reclamation.[c] One, a sample from North Yakima, Wash.,[d] was from the surface 8 inches of the experimental tract north of Wide Hollow Creek. The second sample,[e] from the Toft-Hansen tract at Fresno, Cal., was from the upper 8 inches of soil in a spot plainly showing "black alkali" at the surface. When collected there were only a few scattering spears of grain on this spot, although all about it the grain had made a good stand. When the crust formed by the "alkali" was broken, grain was found which had sprouted but had not been able to push through the crust. A calcium carbonate hardpan occurred about 3 feet below the surface, but was also found at the same depth in adjoining fields on which there was a good stand of barley.

Chemical analyses of the water-soluble salts in these samples by the conventional method[f] of digesting the sample with five times its weight of water gave the results shown in Table XVI. It will be observed that both samples were of the same type of alkali soils, containing, besides the soluble carbonates, notable quantities of sodium sulphate, with much less amounts of other sulphates and chlorides.

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[a] See Bul. No. 30, Bureau of Soils, U. S. Dept. Agr., 1905.

[b] Jour. Am. Chem. Soc., 28, 1639 (1906).

[c] Bul. No. 42, Bureau of Soils, U. S. Dept. Agr., 1907.

[d] Sample No. 14413, Bureau of Soils collection.

[e] Sample No. 14402, Bureau of Soils collection.

[f] Bul. No. 18, p. 65, Bureau of Soils, U. S. Dept. Agr., 1901.

From the mechanical analyses of these samples (Table XVII), together with their field properties, both the Yakima and Fresno soils would be classified as fine sandy loams.

TABLE XVI.—*Water-soluble constituents in soils from North Yakima, Wash., and Fresno, Cal., extracted by digesting one part of soil with five parts of water.*

Constituent.	North Yakima.	Fresno.	Constituent.	North Yakima.	Fresno.
	Per cent.	*Per cent.*		*Per cent.*	*Per cent.*
Ca	Tr.	Tr.	Cl	0.03	0.03
Mg	0.02	Tr.	HCO_3	.27	.16
Na	.24	0.13	CO_3	.10	.02
K	.03	.02			
SO_4	.18	.09	Total	.87	.45

TABLE XVII.—*Mechanical analyses of soils from North Yakima, Wash., and from Fresno, Cal.*

Conventional name.	Diameter.	North Yakima.	Fresno.
	mm.	*Per cent.*	*Per cent.*
Fine gravel	2 to 1	Tr.	0.1
Coarse sand	1 to 0.5	1.3	2.1
Medium sand	0.5 to 0.25	2.5	3.7
Fine sand	0.25 to 0.01	12.8	24.7
Very fine sand	0.01 to 0.05	21.2	33.6
Silt	0.05 to 0.005	48.6	29.5
Clay	0.005 to 0	13.5	6.2

EXPERIMENTAL METHODS.

The method of percolation was essentially the same as that employed by Schreiner and Failyer,[a] with the exception that a constant water pressure was maintained instead of keeping the rate of percolation constant. One hundred grams of soil were placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, and distilled water allowed to percolate through the soil under a constant water pressure of 199 cm., or 6.5 feet.

The volume of each percolate was measured, its electrical conductivity taken with a field bridge,[b] and its time of flow recorded. Normal carbonates (CO_3) and bicarbonates (HCO_3) were then determined volumetrically with standard acid potassium sulphate solution and the chlorine titrated with tenth normal silver nitrate solution, using potassium chromate as indicator. Sulphates were not determined, because the amounts here involved are too small to have any great agricultural significance and the analytical difficulties in handling quantities of this magnitude would be unjustifiably great.

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[a] Jour. Phys. Chem., **10**, 239, 361 (1906). Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906.

[b] Bul. No. 15, Bureau of Soils, U. S. Dept. Agr., 1899, p. 15.

RESULTS WITH SOIL FROM NORTH YAKIMA.

The data obtained with the Yakima soil are given in Table XVIII. The first column gives the time during which percolation has been progressing; the second column, the total volume of percolate; the third column, the conductivity of the successive percolates, at 25° C., expressed in reciprocal ohms multiplied by 1,000, which may be converted to "specific conductivity" by multiplying by the cell factor, 3.57. The next three columns give concentrations in the successive leachings, and the last three columns show the total amounts of the several constituents removed from the soil.

Table XVIII.—*Extraction of alkali salts from North Yakima soil by leaching.*

Time.	Volume of percolate passed.	Conductivity of successive portions of percolate × 10^3. T=25° C.	Concentration of successive portions of percolate in ppm. of solution.			Total quantity of constituents leached from 100 grams of soil.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
Hours.	*C. c.*	*Ohms.*	*Ppm.*	*Ppm.*	*Ppm.*	*Gram.*	*Gram.*	*Gram.*
48	37	....	84	1,160	193	0.00304	0.0424	0.00715
120	101	....	196	1,586	110	.0156	.1439	.01420
216	170	5.76	171	753	152	.0274	.1962	.02470
264	242	3.62	223	406	4	.0433	.2252	.02498
312	312	4.07	168	445	2	.0550	.2563	.02512
360	383	3.98	128	403	3	.0641	.2849	.02533
432	473	3.38	89	385	4	.0722	.3199	.02569
480	539	2.94	64	388	4	.0764	.3451	.02595
558	629	2.80	73	321	1	.0829	.3740	.02607
726	739	2.49	73	263	0.7	.0909	.4029	.02615
778	829	2.17	73	218	Tr.	.0974	.4225	....
827	917	2.04	67	221	....	.1034	.4420	....
873	992	1.90	78	158	....	.1093	.4538	....
940	1,097	1.71	78	130	....	.1173	.4675	....
988	1,184	1.77	50	170	....	.1219	.4823	....
1,065	1,314	1.63	42	185	....	.1273	.5065	....
1,114	1,398	1.51	34	164	....	.1301	.5203	....
1,163	1,485	1.33	22	170	....	.1322	.5352	....
1,210	1,562	1.24	27	145	....	.1343	.5470	....
1,259	1,642	1.03	22	127	....	.1361	.5583	....
1,306	1,716	1.03	6	139	....	.1365	.5683	....
1,378	1,831	1.00	8	130	....	.1372	.5733	....
1,443	1,951	.91	11	109	....	.1385	.5864	....
1,499	2,050	.93	11	115	....	.1396	.5978	....
1,566	2,138	.83	8	103	....	.1404	.6069	....
1,614	2,216	.74	6	94	....	....	.6142	....
1,665	2,306	.71	6	85	....	....	.5214	....
1,711	2,378	.68	6	79	....	....	.6271	....
1,785	2,490	.61	6	73	....	....	.6353	....
1,836	2,586	.59	0	79	....	....	.6429	....
1,884	2,673	.59	0	67	....	....	.6487	....
1,932	2,768	.51	0	67	....	....	.6551	....
2,004	2,908	.45	0	67	....	....	.6645	....
2,076	3,028	.48	0	61	....	....	.6718	....
2,148	3,148	.43	0	55	....	....	.6784	....
2,340	3,378	....	0	51	....	....	.6900	....
2,460	3,583	....	0	47	....	....	.6996	....
2,580	3,813	.51	....	42	....	....	.7093	....
2,772	4,088	....	....	42	....	....	.7209	....
2,887	4,276	....	....	39	....	....	.7283	....
3,007	4,526	.48	....	36	....	....	....	....
3,125	4,741	.49	....	36	....	....	....	....
3,246	4,941	.49	....	33	....	....	....	....
3,391	5,201	.44	....	24	....	....	....	....
3,583	5,528	.53	....	9	....	....	....	....
3,803	5,958	.39	....	18	....	....	....	....
3,899	6,142	.42	....	18	....	....	....	....

An inspection of the results presented in Table XVIII shows that while the water passing through the soil is kept under a constant head the rate of percolation is not constant, but varies somewhat from time to time. The first water entering the dry soil runs through quite rapidly, but as soon as the soil becomes saturated it moves much more slowly. Variations in the rate of percolation are subsequently observed, due undoubtedly in some cases to "channeling" in the soil, in some cases probably to "silting up" of channels, and in other cases partly to the fact that as the percolation proceeds the strongly deflocculating action of the alkali diminishes as its quantity decreases, so that the soil behaves as if it suffered a change in texture as well as in structure. For these reasons the concentrations of the successive portions of the percolates, as evidenced by the conductivity as well as by the analyses, do not show a *regularly* progressive change, although on the whole the concentrations become lower and lower as percolation proceeds. These results are in harmony with many field observations where it has been found that the concentration of a drainage water may vary over quite a wide range, depending upon the rate at

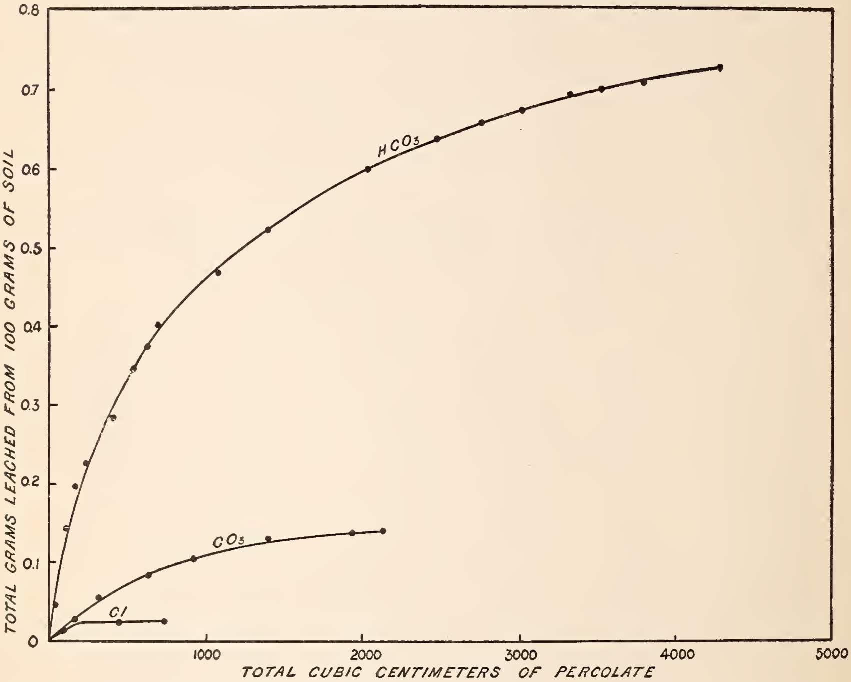

FIG. 3.—Curve showing the total quantities of carbonates, bicarbonates, and chlorine removed by percolating North Yakima black alkali soil with distilled water.

which the applied water moves through the soil and upon the length of time of contact between the water and soil, since considerable time is necessary for equilibrium to result between the salts dissolved and those remaining in the soil.[a]

In the present case chlorides had practically disappeared after 778 hours, when 829 c. c. of water had passed through the soil. Normal carbonates failed to appear in the percolate after 1,614 hours, when 2,216 c. c. of solution had passed. This does not mean, however, that no normal carbonates remained in the soil, for, as has been previously shown in this laboratory,[b] dilution of a normal carbonate causes a change with formation of bicarbonate. It is certain that after 1,614 hours the amount of normal carbonates in the solution has been reduced to a point below that dangerous to plant growth. The alkali, in the form of bicarbonates, however, continued to be leached from the soil after percolation had proceeded for 120 days and a total volume of over 4,200 c. c. had passed through the soil. The results are readily seen in figure 3, where the abscissas are total volume of percolate and the ordinates total grams of the several constituents removed from the soil. The curves are all asymptotic. In the case of the chlorides and normal carbonates, as noted above, the amounts in the successive portions of percolate soon become too small to determine accurately; but in the case of the bicarbonate, amounts could still be readily determined, while the run of the figures in the table and the shape of the curve show that at the termination of the experiment the amount in the successive portions of percolate was slowly diminishing. This is brought out more

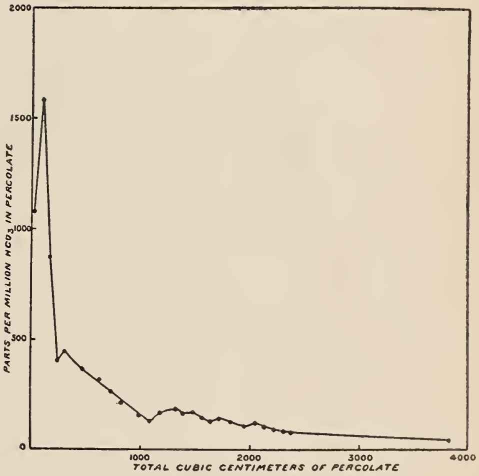

FIG. 4.—Curve showing the quantity of bicarbonate in solution in the successive percolates when North Yakima black alkali is leached with distilled water.

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[a] Bul. No. 33, Bureau of Soils, U. S. Dept. Agr., 1906, and Jour. Am. Chem. Soc., 28, 1229 (1906).

[b] Bul. No. 18, Bureau of Soils, U. S. Dept. Agr., 1901; Jour. Phys. Chem., 5, 537 (1901).

clearly in figure 4, in which the ordinates represent the concentrations in parts per million in successive portions of the percolate. This result is analogous to former leaching experiments made in this laboratory. An inspection of the results for bicarbonates shows, moreover, that if the first few observations be disregarded the leaching curve is described with fair accuracy by the equation

$$\frac{dy}{dv} = K(A-y)$$

proposed by Schreiner and Failyer.[a]

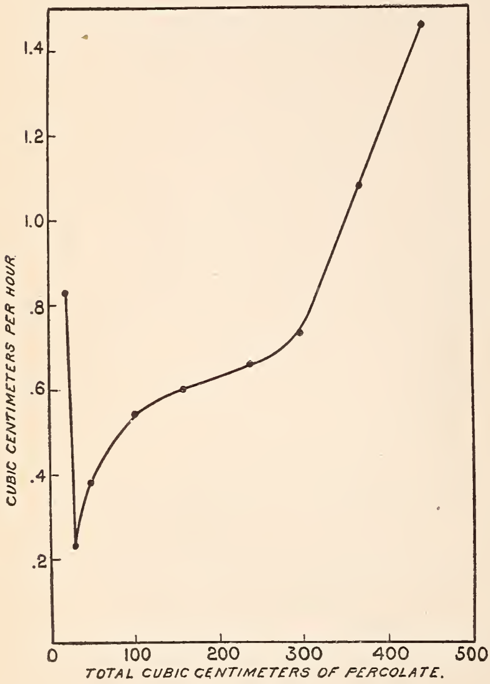

FIG. 5.—Curve showing the progressive change in the rate of percolation as the soluble salts are extracted from Fresno black alkali soil by distilled water.

RESULTS WITH SOIL FROM FRESNO.

In working with the Fresno sample the same experimental difficulties were encountered as with the Yakima sample, in that changes in flocculation and channeling materially affected the rate of leaching. In Table XIX are given the rates of leaching during the earlier part of the experiment. The results are more clearly shown in figure 5. It is seen that at first there is a rapid fall in the rate, and then as percolation proceeds, with the formation of channels and an increase in the flocculation due to the partial removal of the alkali, there is an increase in the rate of percolation, becoming quite regular after about 300 c. c. have passed through the soil. It is believed that these changes in the physical condition of the soil as affecting percolation in these experiments are very helpful in showing what may be expected in field practice, although it must be remembered that the intermittent leaching to which the soil is subjected in the field should be more effective than the laboratory results, at least in so far as respects the volume of water required.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906.

In Table XX are given the data obtained from the leachings of the Fresno soil, which are also shown in figures 6 and 7.

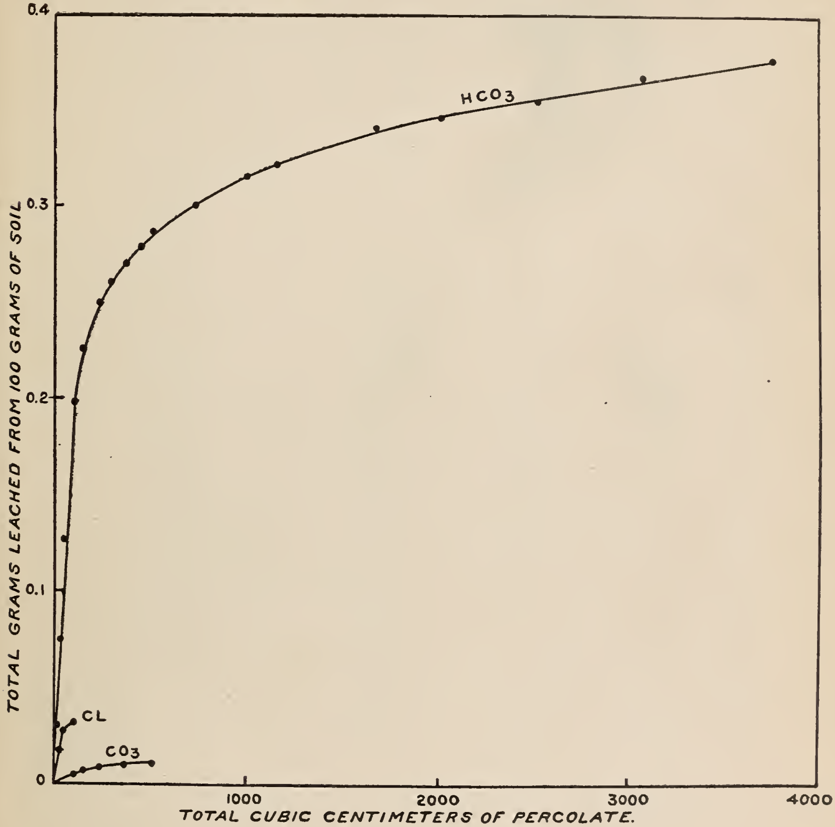

FIG. 6.—Curve showing the total quantities of carbonates, bicarbonates, and chlorine removed by percolating Fresno black alkali soil with distilled water.

TABLE XIX.—*Rate of leaching through soil from Fresno.*

Total percolate.	Quantity per hour.	Total percolate.	Quantity per hour.	Total percolate.	Quantity per hour.
C. c.	*C. c.*	*C. c.*	*C. c.*	*C. c.*	*C. c.*
20	0.83	101	0.54	295	0.73
31	.23	159	.60	368	1.08
49	.38	238	.66	443	1.46

TABLE XX.—*Extraction of alkali salts from Fresno soil by leaching.*

Time.	Volume of percolate passed.	Conductivity of successive portions of percolate $\times 10^3$. T=25° C.	Concentration of successive portions of percolate in p.p.m. of solution.			Total quantity of constituents leached from 100 grams of soil.		
			CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
Hours.	*C. c.*	*Mhos.*	*P.p.m.*	*P.p.m.*	*P.p.m.*	*Gram.*	*Gram.*	*Gram.*
24	20	....	....	1,514	352	....	0.0303	0.0070
72	31	....	....	4,125	961	....	.0757	.0176
120	49	....	....	2,860	489	....	.1268	.0264
216	101	7.87	81	1,370	101	0.0042	.1981	.0317
312	159	3.31	45	475	0	.0068	.2256	....
432	238	2.37	23	297	....	.0086	.2489	....
510	295	1.603	12	206	....	.0092	.2606	....
578	368	1.243	12	137	....	.0100	.2706	....
630	444	.842	3	112	....	.0102	.2791	....
679	514	.680	1	105	....	.0103	.2865	....
724	572	.59	0	79	....	....	.2911	....
791	656	.52	....	73	....	....	..2972	....
839	724	.53	....	67	....	....	.3017	....
916	833	.49	....	64	....	....	.3087	....
964	912	.401	....	55	....	....	.3131	....
1,014	1,000	.366	....	33	....	....	.3160	....
1,061	1,083	.361	....	33	....	....	.3187	....
1,110	1,162	.351	....	33	....	....	.3214	....
1,157	1,230	.376	....	43	....	....	.3242	....
1,229	1,345	.417	....	42	....	....	.3291	....
1,301	1,459	.400	....	42	....	....	.3340	....
1,357	1,558	.370	....	37	....	....	.3376	....
1,424	1,667	.334	....	27	....	....	.3406	....
1,472	1,744	.307	....	21	....	....	.3422	....
1,523	1,829	.312	....	19	....	....	.3437	....
1,569	1,905	.283	....	15	....	....	.3449	....
1,643	2,017	.296	....	12	....	....	.3462	....
1,694	2,104	.293	....	15	....	....	.3475	....
1,742	2,185	.293	....	18	....	....	.3490	....
1,790	2,271	.292	....	18	....	....	.3506	....
1,862	2,393	.235	....	15	....	....	.3524	....
1,934	2,513	.209	....	15	....	....	.3542	....
2,006	2,626	.202	....	15	....	....	.3559	....
2,198	2,856	....	....	17	....	....	.3598	....
2,318	3,061	....	....	18	....	....	.3635	....
2,438	3,291	.362	....	18	....	....	.3677	....
2,630	3,575	....	....	25	....	....	.3745	....
2,745	3,756	....	....	15	....	....	.3773	....
2,865	3,961	.331	....	9	....	....	....	....
2,983	4,126	.311	....	6	....	....	....	....
3,128	4,346	.451	....	6	....	....	....	....
3,272	4,534	.797	....	6	....	....	....	....
3,468	4,796	.566	....	3	....	....	....	....
3,688	5,136	.859	....	3	....	....	....	....
3,780	5,284	.407	....	3	....	....	....	....

COMPARISON OF RESULTS FOR THE TWO ALKALI SOILS.

In general the results for Fresno soil are very similar to those obtained with the heavier soil from Yakima, but, as might reasonably be expected, the soluble salts disappear more rapidly from the lighter soil. It is also worthy of note that in the case of the Fresno soil the curve for chlorides (fig. 6) lies above that for normal carbonates, while the reverse is the case with the Yakima soil (fig. 3); but this is not a case of selective absorption, for the Yakima soil contained, initially, much more of the carbonates than did the Fresno sample, while both contained approximately the same quantities of chlorides. Further, the later leachings are more dilute than in the case of the heavier Yakima soil, indicating that the latter possesses a higher absorptive power.

The leachings from the two soil samples here described have resulted in the removal of larger total quantities of soluble salts than is indicated by the standard method of analysis. The quantity of carbonates removed by the leaching process agrees, within the limits of experimental error, with the amounts found by digesting the soil with five times its weight of water. In the case of normal carbonates the continuous leachings as compared with the digestion used in the analytical procedure, showed slightly more in the Yakima soil and somewhat less in the Fresno sample. The differences are, however, so small as to be quite possibly ascribed to analytical errors. But it should be remembered that the addition of much water has the effect of converting a part of the normal carbonates into bicarbonates, and it is in respect to this constituent that the leaching process yields much higher results than does the empirical analytical method, which can not take cognizance of absorption effects. The results on the whole indicate that the empirical procedure with the known inherent defects nevertheless gives a very fair idea of the soluble constituents of the soil where the generally impracticable method of leaching can not be employed.

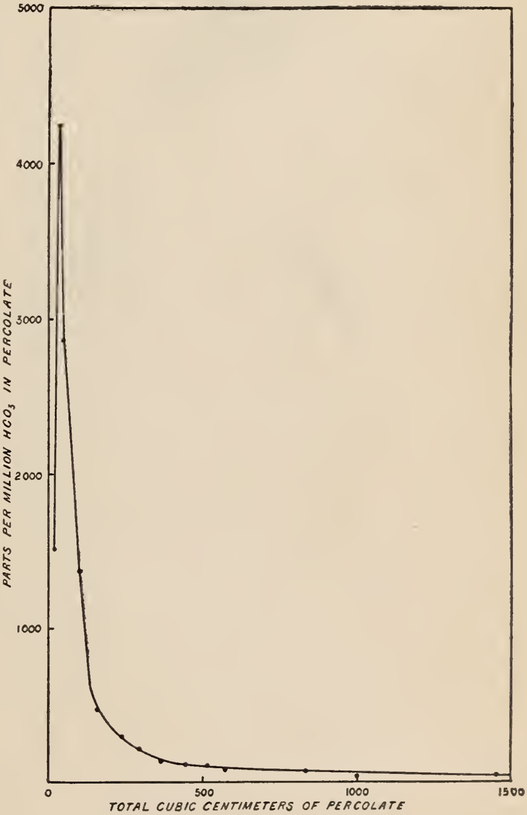

FIG. 7.—Curve showing the quantity of bicarbonate in solution in the successive percolates when Fresno black alkali soil is leached with distilled water.

During the latter half of each percolation experiment the conductivities of the successive percolates show irregular deviations from a fairly constant value, while the titration number for successive percolates slowly diminishes. In the case of the North Yakima soil this mean value of the conductivity, and also the titration numbers, are somewhat higher than for the Fresno soil.

The leaching results presented above indicate the following conclusions: Neutral salts, such as chlorides, in the presence of carbonates are comparatively easy to leach from the soil. With continued leaching of the soils containing "black alkali" there is an increase in the rate at which percolation takes place, due probably to the reduction of the amount of alkali present and to a consequent effect on the physical structure of the soil. With continued leaching there is a comparatively rapid reduction of normal carbonates in the soil water, due in large measure to conversion to bicarbonates. Bicarbonates are rapidly removed at first and then continue to be slowly removed in the soil water in very small quantities, diminishing for an indefinite period. The leaching curves conform fairly well to the rate equation, $\frac{dy}{dv} = K(A-y)$, proposed by Schreiner and Failyer. Soils containing "black alkali" can be reclaimed by leaching (i. e., flooding with underdrainage), but the time and amount of water required is probably much greater than in the case of "white alkali."

EFFICIENCY OF CALCIUM SULPHATE IN REMOVING BLACK ALKALI.

Calcium sulphate has been proposed as a remedy for the injurious effect of black alkali upon growing plants. In order to test the effect of calcium sulphate upon the removal of sodium carbonate and bicarbonate under percolation conditions, four experiments were undertaken. In experiments (1) and (3) of Table XXI, 100 grams of the natural alkali soils from North Yakima, Wash., and from Fresno, Cal., were used. Part of each soil in dry powder (70 grams) was slowly poured into the brass percolation tube and allowed to settle down through the water in it and form a percolation bed. The remainder (30 grams) was meanwhile rubbed up with 10 grams of calcium sulphate and then poured into the tube with the rest of its sample, where it settled, forming a top layer rich in calcium sulphate. Distilled water was then added from time to time, replacing that which passed through the soil. The presence of the calcium sulphate was immediately evident from the rapidity with which the solution passed down through the soil, whereas the untreated natural alkali soils when moistened puddle immediately and in the apparatus used in this work require several feet of water head to produce percolation.

A separate series of experiments, carried out under equilibrium conditions with the North Yakima soil, showed that when the theoretical amount of calcium sulphate required to react with the carbonate and bicarbonate is added and rubbed into the soil, and the soil shaken with water and allowed to settle, the sediment thus obtained occupies a greater volume than that for greater or less additions of the calcium sulphate. This maximum point is as yet not so definitely determined as the above statement might indicate, but nevertheless shows the effect of calcium sulphate upon the *volume* and *openness* of this soil when saturated with water, as it is in the percolation tube. A similar series of experiments with the Fresno soil gave corresponding results, but here the maximum volume of sediment was not reached until *three* times the quantity of calcium sulphate equivalent to the carbonates and bicarbonates in the soil had been added. Experiments (2) and (4) were likewise made with the Yakima and Fresno soils, the experimental conditions being the same as in experiments (1) and (3), save that sodium chloride was added to each soil in sufficient quantity to bring its percentage content up to that of an average black alkali sample from the particular locality to which each soil belongs. This was necessary since these samples proved low in chlorides, and it was desirable to use them in this work because their loss of carbonates and bicarbonates had been already determined under known percolation conditions, and could serve for comparison with this similar series in which calcium sulphate is present.

The sodium chloride was added dry to the alkali soils, rubbed up, water added to make a paste, the soil allowed to dry, and again broken up; calcium sulphate was then worked into the top 30 grams as for experiments (1) and (3).

TABLE XXI.—*Effect of calcium sulphate upon the removal of black alkali by leaching.*

Soil.	Volume of percolate passed.	$CaSO_4$ added.	NaCl added.	Concentration of percolate.			Total constituents leached from 100 grams soil.		
				CO_3.	HCO_3.	Cl.	CO_3.	HCO_3.	Cl.
	C. c.	*Grams.*	*Grams.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*Grams.*	*Grams.*	*Grams.*
North Yakima	30	10	....	69	656	....	0.002	0.0197	....
	86	....	....	0	468	....	.002	.0459	....
	267	....	....	....	193	....	.002	.0909	....
	296	....	....	....	58	....	.002	.0926	....
	334	....	....	....	40	....	.002	.0936	....
	465	....	....	....	39	....	.002	.099	....
	527	....	....	....	39	....	.002	.1014	....
	730	....	....	....	37	....	.002	.1089	....
	807	....	....	....	51	....	.002	.1148	....
	951	....	....	....	40	....	.002	.1206	....
Do	30.5	10	0.75	....	223	6,560	....	.0068	0.2002
	45	....	....	10	142	4,780	.00015	.0089	.2672
	177	....	....	60	182	1,333	.008	.0125	.4427
	230	....	....	60	197	42	.0112	.0229	.465
	333	....	....	45	91	10	.0158	.0323	.466
	381	....	....	....	76	0	....	.0360	....
	426	....	....	....	47	0	.0158	.0428	.466
Fresno	13.5	10	....	....	1,400	....	....	.0189	....
	34	....	....	....	1,515	....	....	.0492	....
	144	....	....	....	223	....	....	.0738	....
	296	....	....	....	46	....	....	.0808	....
	415	....	....	....	42	....	....	.0856	....
	573	....	....	....	52	....	....	.0938	....
	672	....	....	....	49	....	....	.0984	....
Do	15	10	.335	....	263	10,640	....	.0039	.1596
	122	....	....	15	136	5,250	.0016	.0185	.7216
	173	....	....	....	53	21	....	.0202	.7323
	281	....	....	....	44	0	....	.0250	....
	316	....	....	....	43	0	....	.0265	....
	450	....	....	....	45	0	.0016	.0326	.7323

The headings of Table XXI are self-explanatory. Table XXII contains a summary of the most important points brought out in Table XXI and in the leaching experiments on these soils, already given, using only distilled water.

For the North Yakima soil containing gypsum the quantity of carbonates in the successive percolates decreased continually, whereas in the natural alkali soil an intermediate portion of the percolate had the highest content. Furthermore, the concentration of bicarbonate in the percolates from the soil treated with calcium sulphate were many times lower than the corresponding concentration of the percolate from the untreated soil.

Moreover, using distilled water alone 2,490 c. c. were passed before all the normal carbonate was leached; but with calcium sulphate present, all the normal carbonates came out in the first 30 c. c. of percolate, and this volume of liquid is very nearly that required to saturate this soil with water; therefore it is very likely that the calcium sulphate solution from the top layer of soil in the percolation tube did not react with this first percolate to its full extent, but pushed this solution on before it and out of the soil. That some reaction had taken place is shown by the decrease of nearly one-half (43.4 per cent) in the quantity of bicarbonates present in even this first percolate.

Distilled water leached in all 0.7283 gram bicarbonate from the natural soil, while with calcium sulphate present only 0.1206 gram bicarbonate appeared in the filtrate. Using calcium sulphate, only one-tenth of the volume of water was required to reduce the concentration of bicarbonate in the percolate to 40 parts per million. Experiment 2 indicates that the presence of sodium chloride in quantity does not materially reduce the efficiency of calcium sulphate, since the chloride is rapidly removed. After 177 c. c. of percolate had passed the concentration was only 42 parts per million chlorine in solution and after 333 c. c., no chlorine appeared in the runnings.

For the Fresno soil a comparison of the first six percolates of Table XXI with those of Table XX shows that calcium sulphate has reduced the concentration of the carbonates in the percolates far below that from the natural soil.

Here, too, the calcium sulphate maintained an open structure in the soil favorable to a steady percolation; and the ready access of solution to the soil contributes to the completeness of the conversion of the alkaline carbonates in the soil into the slightly soluble calcium carbonate, with the consequent rapid disappearance of bicarbonate and normal carbonate in the percolate as shown in experiments 3 and 4, Table XXI. In both of these experiments the conversion of normal carbonate to calcium carbonate is seen to be very nearly complete since normal carbonate is practically absent from the leachings, where sodium chloride is added; and it was not found, in the percolate where only calcium sulphate had been added to the soil. To reduce the concentration of the percolate from the natural soil to 40 parts per million bicarbonate, required 1,000 c. c. of water; but on adding calcium sulphate only about one-third of this volume of percolate was needed to reach this same concentration of bicarbonate.

The total quantity of bicarbonate leached by 3,756 c. c. of water from the natural soil was 0.3773 gram. When 672 c. c. of water had been passed throuh the soil treated with calcium sulphate, 0.0984 gram bicarbonate had been removed. Supposing that the concentration in succeeding percolates had remained constant at 40 parts per million bicarbonate, and they undoubtedly averaged much below this figure, the passage of 3,084 c. c. additional water would have carried into solution 0.1234 gram of bicarbonate, making in all 0.2218 gram. This is without doubt much higher than experiment would have shown, but even so is 60 per cent of the quantity which was actually washed from the untreated soil.

TABLE XXII.—*Effect of calcium sulphate upon the removal of black alkali by leaching.*

Soil.	Na_2CO_3 added.	$CaSO_4$ added.	NaCl added.	Carbonate.		
				Maximum CO_3 in solution.	Water required to remove CO_3.	Total CO_3 leached (100 gs. soil).
	Grams.	*Grams.*	*Gram.*	*P. p. m.*	*C. c.*	*Gram.*
North Yakima				223	2,490	0.1404
Do		10		69	30	.002
Do		10	0.75	60	333	.0158
Fresno				81	679	.0103
Do		10		0	0	0
Do		10	.335	15	122	.0016

Soil.	Bicarbonate.				Chlorine.		
	Maximum HCO_3 in solution.	Minimum HCO_3 in solution.	Water required to reduce HCO_3 to minimum.	Total HCO_3 leached (100 gs. soil).	Maximum chlorine in solution.	Water required to remove chlorine.	Total chlorine leached.
	P. p. m.	*P. p. m.*	*C. c.*	*Gram.*	*P. p. m.*	*C. c.*	*Gram.*
North Yakima	4,100	39	4,276	0.7283	193	739	0.02615
Do	656	40	334	.1206			
Do	223	47	426	.0428	6,560	333	.466
Fresno	4,125	33	1,014	.3773	101	216	.0317
Do	1,515	46	296	.0984			
Do	263	45	450	.0326	10,640	173	.7323

The presence of sodium chloride in Yakima black alkali soil causes decrease in the quantity of bicarbonates which must be leached before the percolates reach a concentration below that dangerous to plants. When above 400 c. c. of the liquid had percolated, the solution had reached a fairly steady concentration. At this point over 0.09 gram of bicarbonate has been leached from the soil containing no additional sodium chloride, whereas the same volume of percolate removed about 0.04 gram of bicarbonate from the soil which had been treated with gypsum and sodium chloride. The same phenomenon is met in the case of the Fresno soil. In the case of the Yakima soil the increase in the bicarbonate in the percolates is evidently due to the rapidly decreasing quantity of sodium chloride present. For both soils the final removal of sodium chloride is accompanied by an almost abrupt drop in the concentration of the percolate with respect to bicarbonate.

In conclusion, these experiments indicate that the use of gypsum facilitates the removal of black alkali from soil, although at the same time it adds to the total quantity of alkali present.

ABSORPTION OF POTASSIUM FROM CARBONATE SOLUTION.

The problem of absorption of salts by soils has been studied not only by percolating natural alkali soils with distilled water, determining the quantity of salts removed, but also by the absorption of salt from a percolating salt solution. After introducing into the soil in this manner a considerable quantity of the alkali salt, thus simulating an alkali soil, percolation was commenced with distilled water.

In the following experiments upon the removal and absorption of a base by a soil, a potassium salt was used rather than a sodium salt, on account of the experimental difficulty of determining small quantities of sodium in solution. The normal carbonate of potassium was chosen because previous work gives the form of the curves for the removal of carbonate. The alkaline carbonates, unlike chlorides and phosphates, which were studied by Schreiner and Failyer,[a] have an enormous influence upon the physical condition of the soil.

The experimental difficulty is not so much to regulate the rate of percolation or to keep it sufficiently slow, as to get the solution through the soil at all. One hundred grams of each soil was placed in a paraffined brass tube fitted below with a short section of a Pasteur-Chamberland filter tube, as already described. The solution was percolated through the soil under a head of 6.5 feet water pressure aided by nearly an atmosphere of suction from a filter pump applied below. This pressure was just sufficient for the needs of the experiment.

Four soils, Galveston clay, Marshall silt loam, Hagerstown loam, and Norfolk sand, were percolated with a solution of potassium carbonate containing 444 parts potassium per million parts of solution, and the potassium in the percolates determined colorimetrically[b] for low concentrations and gravimetrically as the chlorplatinate, when the fractions became stronger. The results are given in Tables XXIII to XXVI, and shown graphically in figure 8, which represents the curves of absorption up to the maximum of each, and from that point on the leaching process appears. The data for these leaching curves are contained in Tables XXVII, XXVIII, and XXIX. Each curve in figure 8 gives the total grams of potassium contained by 100 grams of soil—air-dry weight—at each stage of the absorption process.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., 1906; Jour. Phys. Chem., **10**, 239, 361 (1906).

[b] Bul. No. 31, Bureau of Soils, U. S. Dept. Agr., 1906.

The Galveston clay is still absorbing potassium after five months' continuous percolation, during which time 1.13 per cent of potassium has been absorbed by the soil and the concentration of the percolate with respect to potassium has risen to a little over one-third of that for the solution added to the clay, so that we may expect a very considerable quantity of potassium to be absorbed on further percolation. But it seemed inadvisable to prolong the experiment, since the clay had been shown to have a very high absorptive capacity for potassium and would require a very long time for saturation and for subsequent removal of the salts by percolation. Further points on the curve could give, in addition, only the value of the specific absorptive capacity, from a solution of this concentration. This

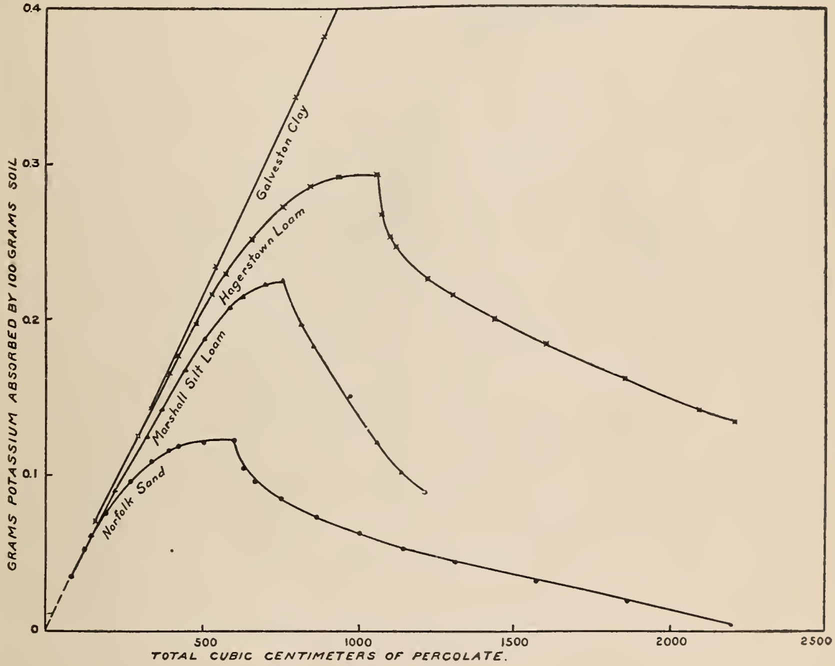

FIG. 8.—Curves showing the total quantity of potassium absorbed from potassium carbonate solution percolating through soils, and the subsequent removal of this absorbed potassium by leaching with distilled water.

absorptive capacity is known for the three other soils used, and the formula $\frac{dy}{dv}=K(A-y)$ proposed by Schreiner and Failyer may be applied.

Table XXIV shows that after some 750 c. c. of the potassium carbonate solution has passed through Marshall silt loam the soil has taken up very nearly all the potassium that it can absorb from a solution of the strength used. Here A, the absorptive capacity of Marshall silt loam for potassium—from this particular concentration of aqueous potassium carbonate—may be taken as 0.230 gram potassium per 100 grams soil. Using this value for A, the results given in Table XXIV conform well to the rate equation of Schreiner and Failyer, $\frac{dy}{dv}=K(A-y)$. For Hagerstown loam, Table XXV, the absorptive capacity, A, is 0.300 gram potassium per 100 grams soil, and the rate of absorption conforms to Schreiner and Failyer's formula, as is also the case for Norfolk sand, whose A, is 0.1226 gram potassium per 100 grams soil, as shown in Table XXVI.

Comparing the soils we see that Hagerstown loam absorbs 0.300 gram, Marshall silt loam 0.230 gram, and Norfolk sand 0.123 gram of potassium per 100 grams of soil. These absorptive capacities are not directly proportional to the areas of the soils per gram as calculated from the mechanical analysis already given.

The absorptive capacity of a soil for potassium from potassium carbonate solution is greater than from potassium chloride solution. Schreiner and Failyer[a] give 1,000 parts per million potassium as the A, for a clay soil in chloride solution containing 200 parts per million potassium; and 650 parts per million as the A for a clay loam under the same conditions. This is a percentage of 0.1 and 0.065, respectively, while Galveston clay absorbed 1.13 per cent, Marshall silt loam 0.23 per cent, Hagerstown loam 0.30 per cent, and Norfolk sand 0.123 per cent potassium—reckoned on the air-dry weight of the soils—from carbonate solution. It is to be remembered that this carbonate solution was more than twice as strong with respect to potassium as the chloride solution used by Schreiner and Failyer. But even taking account of this factor the soils are seen to abstract relatively more potassium from carbonate solution than from chloride solution.

In columns 4 and 5 of the Tables XXIII to XXVI are given the rates of absorption in grams potassium per 100 grams soil per hour, and the rates of percolation in cubic centimeters per hour. The data show a steady decrease in rate of flow as percolation proceeds till a state is reached where the soils seem to form channels and allow the solution to filter faster, and then to close these channels and retard the flow of liquid so that its rate of percolation returns nearly to that prior to the formation of the channels. The initial decrease in rate of flow is not due to packing down of the soils, since they were percolated with distilled water for weeks before any of the potassium carbonate was run through them, but to the puddling or deflocculation produced by the alkaline solution. After the soil is impregnated with alkali the passage of the strong potassium carbonate solution through it is faster than the subsequent flow of distilled water, but as the potassium is washed out the rate increases again.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. of Agr., 1906, p. 37; Jour. Phys. Chem., **10**, 361 (1906).

This may be referred to the flocculating and deflocculating action upon the soil grains by the same solute at different concentrations, which has been discussed previously. The production of large floccules would of course permit the solution to pass through more readily and the subsequent breaking down into smaller aggregates would offer a much less permeable percolation bed.

At the beginning of leaching it was necessary to subject the Hagerstown loam to suction under a force of about an atmosphere in addition to the constant head of water, but as leaching proceeded this suction was removed to avoid too rapid percolation. Consequently the rate of percolation for this soil as given in column 5 of Table XXVIII is not exactly comparable with the similar data in Tables XXVII and XXIX. This set of figures on the rate of percolation enables one to compare the rate of absorption with the rate of flow.

The continual decrease in the rate of removal of potassium from these three soils as shown in figure 8, and in the concentration of the percolates given in Tables XXVII, XXVIII, and XXIX, is similar to that for the removal of carbonate, bicarbonate, and chlorine from the natural alkali soils of Yakima and Fresno.

The removal of potassium absorbed by soil from a carbonate solution gives a leaching curve closely resembling that for the removal of potassium absorbed from chloride solution.[a]

The absorption of potassium from carbonate and from chloride solution is likewise described by curves similar in form, and very nearly represented by the formula $\frac{dy}{dv} = K(A-y)$, which also expresses well the rate of absorption and rate of removal of the phosphate radical, PO_4, from soils[a] regardless of what phosphate was used to saturate the soil.

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[a] Bul. No. 32, Bureau of Soils, U. S. Dept. Agr., p. 36.

TABLE XXIII.—*Absorption of potassium from carbonate solution by Galveston clay.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
15	13	0.0065	0.00043	1.00	15.0
25	13	.0108	.00062	1.44	21.9
54	13	.0232	.00062	1.45	41.9
90	9	.0388	.00063	1.46	66.7
158	14	.0679	.00066	1.54	110.9
199	14	.0855	.00066	1.54	137.5
228	16	.0978	.00066	1.54	156.2
271	15	.1162	.00067	1.56	183.8
297	14	.1273	.00068	1.57	200.3
335	15	.1435	.00067	1.57	224.5
411	14	.1707	.00067	1.58	272.5
465	15	.1992	.00069	1.57	305.8
545	17	.2332	.00065	1.53	358.1
802	19	.3423	.00054	1.38	445.6
896	24	.3818	.00054	1.29	518.6
993	32	.4217	.00050	1.22	598.1
1,043	34	.4422	.00048	1.17	640.9
1,168	58	.4904	.00048	1.24	741.9
1,248	76	.5198	.00042	1.16	811.2
1,363	63	.5615	.00044	1.21	906.5
1,464	90	.5970	.00037	1.06	1,002.2
1,566	102	.6319	.00035	1.02	1,102.2
1,663	80	.6671	.00038	1.05	1,194.2
1,763	72	.7042	.00039	1.04	1,260.2
1,868	73	.7431	.00031	.84	1,385.2
1,925	175	.7564	.00020	.84	1,453.2
2,033	102	.7933	.00029	.86	1,578.2
2,154	165	.8270	.00023	.83	1,724.2
2,294	186	.8632	.00022	.82	1,896.2
2,429	167	.9005	.00022	.81	2,073.7
2,582	113	.9512	.00026	.80	2,266.7
2,711	152	.9891	.00020	.68	2,458.2
2,860	149	1.0331	.00029	.71	2,670.0
2,949	170	1.0574	.00009	.54	2,835.5
3,043	195	1.0808	.00005	.22	3,268.0
3,105	178	1.0972	.00011	.42	3,415.0
3,213	145	1.1294	.00017	.56	3,607.0

TABLE XXIV.—*Absorption of potassium from carbonate solution by Marshall silt loam.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
48	7	0.0210	0.00088	2.00	24
145	24	.0615	.00169	4.00	48
225	83	.0904	.00120	3.33	72
325	94	.1254	.00100	2.85	107
372	95	.1418	.00068	1.96	131
403	97	.1526	.00065	1.86	148
445	98	.1674	.00062	1.77	172
469	100	.1757	.00052	1.53	188
508	135	.1877	.00034	1.29	223
558	189	.2004	.00026	1.04	271
590	244	.2066	.00013	.66	319
630	275	.2140	.00016	.87	365
676	318	.2198	.00008	.64	437
696	350	.2217	.00004	.42	485
732	390	.2237	.000028	.50	557
756	400	.2248	.000023	.50	605

TABLE XXV.—*Absorption of potassium from carbonate solution by Hagerstown loam.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
160	6	0.0700	0.00291	6.68	24
292	23	.1245	.00226	5.5	48
392	43	.1648	.00165	4.14	72
478	75	.1966	.00065	1.79	120
530	97	.2146	.00075	2.16	144
573	115	.2287	.00059	1.79	168
630	167	.2445	.00066	2.37	192
657	200	.2513	.00028	1.14	216
696	215	.2602	.00039	1.62	240
753	240	.2718	.00024	1.19	288
796	275	.2790	.00016	.90	336
845	301	.2857	.00015	1.09	380
902	360	.2907	.00007	.80	452
934	406	.2919	.000025	.67	500
983	424	.2929	.000014	.67	572
1,016	428	.2934	.000011	.69	620

TABLE XXVI.—*Absorption of potassium from carbonate solution by Norfolk sand.*

[100 grams soil. Solution containing 444 parts per million potassium.]

Total percolate.	Potassium in percolate.	Potassium absorbed by 100 grams soil.	Rate of absorption.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Grams.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
82	5	0.0360	0.00015	3.39	24
122	37	.0523	.000068	1.69	48
193	107	.0762	.0000996	2.96	72
274	193	.0966	.0000425	1.69	120
313	232	.1048	.0000344	1.62	144
338	261	.1098	.0000191	1.04	168
370	305	.1142	.0000183	1.34	192
389	330	.1164	.0000092	.79	216
420	365	.1189	.0000052	1.29	240
464	407	.1205	.0000033	.92	288
502	417	.1216	.0000023	.78	336
546	422	.1226	.0000021	.92	884
600	444	.1226	....	.76	442

TABLE XXVII.—*Leaching of potassium from Marshall silt loam.*

[100 grams, containing 0.2248 gram potassium, absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
0	0	0.2248	....	....	0
17	471	.2168	0.000187	0.354	48
36	513	.2070	.000168	.346	103
59	426	.1972	.000123	.290	183
72	410	.1919	.000125	.304	226
95	375	.1833	.000086	.228	327
125	273	.1751	.000050	.183	492
162	151	.1695	.000053	.386	588
194	273	.1607	.000088	.320	688
217	320	.1533	.000039	.123	876
235	350	.1470	.000033	.094	1.069
256	412	.1383	.000033	.080	1,333
301	278	.1258	.000035	.125	1,693
336	337	.1140	.000030	.091	2,078
369	230	.1064	.000020	.088	2,456
390	190	.1024	.000009	.044	2,889
412	202	.0979	.000031	.150	3,036
435	162	.0942	.000019	.120	3,228
456	166	.0907	.0000185	.111	3,417

TABLE XXVIII.—*Leaching of potassium from Hagerstown loam.*

[100 grams, containing 0.2934 gram potassium absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour.*	*Hours.*
0	0	0.2934			
24	538	.2805	0.00026	0.50	48
51	490	.2673	.00024	.49	103
85	436	.2525	.000107	.43	183
103	311	.2469	.000131	.42	225
144	237	.2376	.000092	.40	326
169	256	.2312	.000093	.36	395
206	145	.2258	.000056	.39	490
243	151	.2202	.000058	.39	586
280	133	.2153	.000044	.37	686
311	90	.2124	.000030	.34	772
346	107	.2087	.000039	.37	868
393	116	.2032	.000047	.38	994
416	114	.2006	.000039	.34	1,062
460	114	.1956	.000040	.35	1,187
511	100	.1905	.000035	.35	1,333
581	90	.1842	.000033	.36	1,525
637	82	.1796	.000027	.34	1,692
704	82	.1741	.000029	.35	1,885
774	87	.1680	.000032	.37	2,077
841	82	.1625	.000026	.32	2,289
896	76	.1583	.000025	.33	2,455
1,032	83	.1470	.000026	.32	2,887
1,077	89	.1430	.000027	.31	3,034
1,136	75	.1386	.000023	.31	3,226
1,191	82	.1341	.000024	.29	3,415

TABLE XXIX.—*Leaching of potassium from Norfolk sand.*

[100 grams, containing 0.1226 gram potassium absorbed from K_2CO_3 solution.]

Total percolate.	Potassium in percolate.	Potassium left in soil.	Rate of leaching.	Rate of percolation.	Period.
C. c.	*P. p. m.*	*Gram.*	*Gram per hour.*	*C. c. per hour*	*Hours.*
0	0	0.1226			
30	582	.1051	0.000314	0.63	48
67	236	.0964	.000159	.67	103
119	138	.0892	.000091	.66	183
148	125	.0856	.000085	.68	226
219	105	.0781	.000074	.70	327
265	97	.0736	.000070	.67	396
335	71	.0686	.000053	.74	491
403	83	.0630	.000059	.71	587
476	75	.0575	.000055	.73	687
541	63	.0534	.000044	.71	779
616	59	.0490	.000046	.78	875
708	53	.0441	.000039	.74	1,000
759	49	.0416	.000037	.75	1,068
857	48	.0369	.000038	.75	1,193
967	42	.0323	.000032	.92	1,339
1,124	44	.0254	.000040	.81	1,510
1,259	41	.0199	.000041	.80	1,678
1,422	43	.0129	.000043	.85	1,871
1,592	44	.0044	.000039	.89	2,063
1,742	34	− .0007	.000024	.71	2,275
1,897	25	− .0046	.0000236	.94	2,330
2,142	21	− .0083	.000019	.57	2,763
2,322	18	− .0116	.000022	1.22	2,910
2,512	4	− .0124	.000004	.99	3,102
2,707	2	− .0128	.0000019	1.08	3,291

Thus we have shown that the removal curves for bicarbonate, carbonate, chlorine, potassium, and phosphate leached from soils are very similar in form.

It has also been demonstrated by these percolation studies that the absorptive capacity of soils is very considerable, large quantities of both acid and basic radicals being retained. These are again released by the soil to fresh additions of water and to the soil solution, as the plants remove the nutrient salts.

SUMMARY.

In the foregoing pages the work on absorption by soils, which has been in progress in the Bureau for some years, has been continued and a further and more complete study has been made of the composition of the solutions and the quantity of material removed from solution by the soil. The literature upon the subject of absorption has been brought together.

In the experiments described the materials used are not always fertilizer salts or constituents of the soil itself, since other substances, particularly certain dyestuffs, are better adapted to obtaining a more detailed knowledge of the mechanism of absorption. In general, it may now be stated that where disturbing influences are not great the mathematical formulation may be made both of the time rate and of the absorption and distribution of the material between the solid and the liquid. The disturbing influences, however, are quite important in most cases actually met in practice, and therefore a detailed study of some of them was undertaken. The most important of these is the change in the physical character of the soil itself, consequent upon the absorption of the dissolved materials. In some cases, notably with acids and with lime, the soils assume a "flocculated" structure, i. e., a great many of the ultimate grains form larger aggregates or "ball together;" and in other cases, especially with alkalies, the soils are deflocculated, each grain standing out separate and distinct from the others. This change in the structure of the soil is of the utmost importance in influencing the physical condition of the soil, which in turn influences the drainage condition, the aeration of the soil, its capacity to hold the soil solution and control its movement through the soil, the composition of the soil solution, the character and rate of the chemical changes taking place in the soil solution; and, in fact, in influencing directly both the physical and chemical factors which are the most important in governing the proper growth of plants.

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